UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF
PREVENTION, PESTICIDES
AND TOXIC SUBSTANCES

Note to Reader

Background: As part of its effort to involve the public in the implementation of the Food Quality Protection Act of 1996 (FQPA), which is designed to ensure that the United States continues to have the safest and most abundant food supply. EPA is undertaking an effort to open public dockets on the organophosphate pesticides. These dockets will make available to all interested parties documents that were developed as part of the U.S. Environmental Protection Agency's process for making reregistration eligibility decisions and tolerance reassessments consistent with FQPA. The dockets include preliminary health assessments and, where available, ecological risk assessments conducted by EPA, rebuttals or corrections to the risk assessments submitted by chemical registrants, and the Agency's response to the registrants' submissions.

The analyses contained in this docket are preliminary in nature and represent the information available to EPA at the time they were prepared. Additional information may have been submitted to EPA which has not yet been incorporated into these analyses, and registrants or others may be developing relevant information. It's common and appropriate that new information and analyses will be used to revise and refine the evaluations contained in these dockets to make them more comprehensive and realistic. The Agency cautions against premature conclusions based on these preliminary assessments and against any use of information contained in these documents out of their full context. Throughout this process, If unacceptable risks are identified, EPA will act to reduce or eliminate the risks.

There is a 60 day comment period in which the public and all interested parties are invited to submit comments on the information in this docket. Comments should directly relate to this organophosphate and to the information and issues available in the information docket. Once the comment period closes, EPA will review all comments and revise the risk assessments, as necessary.

These preliminary risk assessments represent an early stage in the process by which EPA is evaluating the regulatory requirements applicable to existing pesticides. Through this opportunity for notice and comment, the Agency hopes to advance the openness and scientific soundness underpinning its decisions. This process is designed to assure that America continues to enjoy the safest and most abundant food supply. Through implementation of EPA's tolerance reassessment program under the Food Quality Protection Act, the food supply will become even safer. Leading health experts recommend that all people eat a wide variety of foods, including at least five servings of fruits and vegetables a day.

Note: This sheet is provided to help the reader understand how refined and developed the pesticide file is as of the date prepared, what if any changes have occurred recently, and what new information, if any, is expected to be included in the analysis before decisions are made. **It is not meant to be a summary of all current information regarding the chemical.** Rather, the sheet provides some context to better understand the substantive material in the docket (RED chapters, registrant rebuttals, Agency responses to rebuttals, etc.) for this pesticide.

Further, in some cases, differences may be noted between the RED chapters and the Agency's comprehensive reports on the hazard identification information and safety factors for all organophosphates. In these cases, information in the comprehensive reports is the most current and will, barring the submission of more data that the Agency finds useful, be used in the risk assessments.

Jack E. Housenger, Acting Director
Special Review and Reregistration Division

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REREGISTRATION ELIGIBILITY SCIENCE CHAPTER

FOR

CHLORPYRIFOS

FATE AND ENVIRONMENTAL RISK ASSESSMENT CHAPTER

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C. ENVIRONMENTAL RISK ASSESSMENT

1. Use Characterization

Chlorpyrifos(o,o-diethyl o-(3,5,6-trichloro-2-pyridyl) phosphorothioate, is a broad spectrum, organophosphorus insecticide whose mode of activity is as a cholinesterase inhibitor. Chlorpyrifos is registered for use on a variety of terrestrial food crops, terrestrial food and feed crops, terrestrial non-food crops, greenhouse food/non-food, and domestic indoor and outdoor sites. The number of registered products containing chlorpyrifos is about 1,000 products. Chlorpyrifos is used widely throughout the U.S. There are five manufacturers: DowElanco is supporting the bulk of the uses; Makhteshim-Agan (America), Inc. currently has only one registered use (termiticide), Gharda, Luxemburg-Pamol, and Cheminova. Chlorpyrifos has 7 registered technical products, 30 intermediate formulations and about 900 products.

About 20,960,000 lbs active ingredient are used yearly with about equal poundage used on agriculture and non-agriculture uses. The highest crop use is (about 26 percent of the total volume is applied to 7% of the planted corn acreage). The next seven major crops treated with chlorpyrifos are cotton, apples, alfalfa, citrus, peanuts, pecans and wheat. Chlorpyrifos use on all other crops is less than 2.5 percent of the total pounds of chlorpyrifos applied. Other crops with chlorpyrifos usage over 200,000 lbs ai include alfalfa, apples, corn, cotton, oranges, peanuts, pecans, and wheat. Crops with a high percentage of their total U.S. planted acres treated with chlorpyrifos include brussels sprouts (about 73 %), cranberries (about 46%), apples (about 44%), broccoli (about 41%), cauliflower (31%), and lemons and walnuts (about 30%). The highest use states are California, Washington, Georgia, Florida, Arizona, Nebraska, Iowa, Illinois, and Wisconsin.

Registered non-crop uses of chlorpyrifos include termiticide, turf, golf courses, cattle ear tags, turkey farms, ULV mosquito adulticide, ornamental sites, indoor pest control, and pet tick and flea products, etc.). Approximately 25% of total volume of chlorpyrifos is used for control of subterranean termites. Other major non-agricultural uses include golf courses and turf, indoor, residential perimeter treatments, and ornamentals.

Chlorpyrifos may be applied as spray or as a granular insecticide. The application rates and aerial or ground application vary according to the intended use. According to chlorpyrifos labels, agricultural application rates range from a minimum of 0.25 lbs ai per acre for wheat to a maximum of 11 lbs ai per acre per season for sweet corn in Florida and Georgia. The highest concentration of chlorpyrifos applied as a non-agricultural use is a 2.0 % (20,000 ppm) spray application for termites and a 5,250 ppm formulation sprayed on outside surfaces. Some uses are limited to one application per year, but multiple applications per season are generally registered on labels. The highest number of applications listed on the chlorpyrifos label is up to 22 applications at 0.5 lbs ai/A per growing season on sweet corn in Florida and Georgia. The minimum time intervals between applications on labels range from 3 to 5 days to 60 days. In many cases, the minimum interval between applications is not specified; a 7-day interval is usually used as a default value. The largest crop use of chlorpyrifos is a pre-plant or at-plant soil application with soil incorporation; the maximum label rates are up to 5.0 lb ai/A tobacco. Post-planting applications are up to 2.0 lb ai/A on clover. Foliar spray on orchards is applied by aircraft or ground equipment (directed or airblast); foliar spray rates are up to 6 lb ai/A for aerial and airblast applications on citrus. The most frequent use rate on labels is 1.0 to 2.0 lbs ai/A with one or two applications per year. In general, the major uses that pose the highest potential for risks were also assessed for typical usage (i.e., usually aerial applications on foliage).

Termiticide applications are made by professional applicators; an average application rate for the termiticide is about 10.25 lb/structure as a soil application, either by trenching, rodding, or injection. Sod farm (turf) use is applied at 8 lbs ai/A and nursery fruit trees are up to 4.0 lbs ai/A (Dursban 50W Nursery).

Chlorpyrifos uses have been grouped into ten categories based on similarities in crop grown, field conditions, and non-crop uses. A list of chlorpyrifos uses in each category is provided below.

Group 1. Corn (open ground with enhanced soil erosion)

Group 2. Cover crops (crop cover with reduced soil erosion):
- Alfalfa
- Clover (grown for seed)
- Grass (grown for seed)
- Mint
- Wheat

Group 3. Field crops (open ground with enhanced soil erosion):
- Peanuts
- Cotton
- Sorghum
- Soybeans
- Sunflowers
- Tobacco

Group 4. Vegetables (open ground with enhanced soil erosion):
- Asparagus
- Beans (field, green, kidney, navy, snap, string, & wax)
- Broccoli
- Broccoli raab (rapini)
- Brussel sprouts
- Cabbage
- Carrot (grown for seed)
- Cauliflower
- Chinese broccoli (gai lon)
- Chinese cabbage (bok choy, napa)
- Chinese mustard (gai choy)

Collards
Cucumbers
Kale
Kohlrabi
Mushrooms
Mustard greens
Onions, bulb
Peas (black-eyed, field, and garden)
Peppers
Pumpkins
Radish and Radish (grown for seed)
Rutabagas
Strawberry
Sugar beet and Sugar Beet (grown for seed)
Sweet potato
Tomato
Turnip

Group 5. Citrus Grove Applications (foliar, trunk and grove floor)
(open ground with enhanced erosion)
Citrus
Grapefruit
Lemons
Oranges

Group 6. Fruit and Nut Orchard Applications (dormant, foliar, trunk &/or soil floor)
(ground cover with reduced erosion)
Almonds
Apples
Cherries
Cranberries
Figs
Filberts
Grapes
Macadamia nuts
Nectarines
Peaches
Pears
Pecans
Plums
Prunes
Walnuts
Grapes

Group 7. Livestock Uses
Cattle (ear tags)
Turkey pens (outdoor)

Group 8. Commercial and Residential Uses
Christmas trees (tree farms)
Ornamentals (nursery/landscapers)
Golf courses (turf)
Lawn care (turf)
Residential perimeter pest control
Homeowners (fruit/nut citrus)

Group 9. Termiticide (Structural and Perimeter Treatments)

Group 10. Mosquito adulticide (ULV Treatments)
Urban and Suburban Foggers

Risks to aquatic and terrestrial wildlife have been assessed for most representative uses, except pet products and ear tags. Homeowner uses, ornamentals and applications described as "apply to runoff" have been assessed only for terrestrial risks. Risks for indoor uses have not been assessed for wildlife effects, but some uses, such as the pet shampoos used at kennels and pet grooming shops (a recently canceled use), have been found to pose risks to aquatic areas as indicated by biomonitoring studies. In the past, pet shampoos have been identified as the source of chlorpyrifos in POTW effluents from sewage treatment that exceed discharge permit levels and are toxic to *Ceriodaphnia*, an aquatic invertebrate used in biomonitoring.

In addition to maximum uses rates, BEAD has identified the typical usage for many crops, including the average number of applications, average application rate, number of acres treated, and maximum likely acreage that might be treated. For non-agricultural uses, BEAD reported total active ingredient (lbs ai) used, but did not provide any data on typical use rates. Consequently, risk quotients for non-agricultural uses are limited to assessment of maximum label use rate. The highest typical use rate identified is 2.4 lbs ai/A on citrus. A single seasonal application per year is usually typical for most crops; timing of the application depends upon the intended use. For some crops, the typical use rate includes a second application 20 percent of the time.

2. Exposure Characterization

a. Chemical Profile

Common name: Chlorpyrifos
Chemical name: O,O-diethyl O-(3,5,6-trichloro-2-pyridinyl)phosphorothioate
Trade names: Lorsban, Dursban, Brodan, Eradex, Piridane
Physical/Chemical properties:

Molecular formula:	$C_9H_{11}Cl_3NO_3PS$
Molecular weight:	350.57
Physical state:	White granular crystals
Melting point:	42 - 43.5°C
Vapor Pressure:	1.87×10^{-5} mm Hg at 25°C
Water solubility:	2 mg/L water at 25°C
Henry's Law Constant:	4.2×10^{-6} atm·m^3/mol at 25°C
Log K_{ow}:	4.70

b. Environmental Fate and Transport Data

The environmental fate database for chlorpyrifos is largely complete. The major route of dissipation appears to be aerobic and anaerobic metabolism. Abiotic hydrolysis, photodegradation, and volatilization do not seem to play a significant role in the dissipation process. Based on available data, chlorpyrifos appears to degrade slowly in soil under both aerobic and anaerobic conditions. Information on leaching and adsorption/desorption indicate that parent chlorpyrifos is largely immobile. The environmental fate of the major chlorpyrifos degradate, 3,5,6-trichloro-2-pyridinol (TCP), indicates that it is mobile in soils and persistent in soils when not exposed to light. Available field data indicate that chlorpyrifos has a half-life in the field of less than 60 days, with little or no leaching observed. Because of its low water solubility and high soil binding capacity, there is potential for chlorpyrifos sorbed to soil to runoff into surface water via erosion. Chlorpyrifos has the potential to bioaccumulate in fish and other aquatic organisms and enter the aquatic food web. Chlorpyrifos residues in aquatic species may result in dietary exposure for aquatic birds and mammals feeding on aquatic organisms. Chlorpyrifos rapidly depurates from fish when aquatic chlorpyrifos exposures cease.

The termiticide use of chlorpyrifos has had a significant impact on surface water and ground water quality for some localized wells across the country. In 1993 and 1994, the Agency received several 6(a)2 submissions from DowElanco concerning chlorpyrifos detections in ground water. These detections of chlorpyrifos, all greater than the lifetime Health Advisory level (HAL) of 20 ppb, resulted from Dursban TC and Equity TC termiticide treatments. Chlorpyrifos was detected in drinking water wells at 37 sites in Kentucky, Missouri, Alabama, Tennessee, South Carolina, New York, Ohio, North Carolina, Illinois, Virginia, Maryland, Indiana, and nine unknown locations. Levels of chlorpyrifos in these drinking water wells ranged from 32 ppb up to 2,090 ppb (over 100 times the HAL). Many (43%) of the reported detections were above 100 ppb or five times greater than the HAL for adults. In addition, all of the detections exceeded the one-day child health advisory of 30 ppb.

Contamination of ground water resources can also have an impact on ecological endpoints because of the interaction between ground and surface water. Based on our current knowledge of ecological endpoints, Chlorpyrifos may have an impact on aquatic invertebrates and fish through ground water flow into surface waters, as a seep or spring.

Chlorpyrifos can contaminate surface water at application via spray drift. Substantial fractions of applied chlorpyrifos could be available for runoff for several weeks to months post-application (aerobic soil metabolism half-lives of 11-180 days for 8 soils; terrestrial field dissipation half-lives of 33-56 days). The intermediate to high soil/water partitioning of chlorpyrifos (K_{oc}s of 3680-31,000; SCS/ARS database K_{oc} of 6070; K_ds of 50-260) indicate that most of chlorpyrifos runoff is generally via adsorption to eroding soil rather than by dissolution in runoff water. However, in some cases within the lower ranges of adsorption and when runoff volume greatly exceeds sediment yield, dissolution in runoff water may also contribute significantly to runoff.

I. Degradation

(a) Abiotic Hydrolysis

Hydrolysis of chlorpyrifos in neutral and acidic sterile buffer solutions with half-lives of approximately 72 and 73 days, respectively. In pH 9 solutions the half-life was approximately 16 days. Major degradates, which appear to be resistant to hydrolysis, were TCP and O-ethyl O-(3,5,6-trichloro-2-pyridinol) phosphorothioate, at up to 48 and 13 percent of the applied, respectively. The Hydrolysis (161-1) data requirement is fulfilled (MRID 00155577).

(b) Photodegradation in Water

Photodegradation does not appear to be a major route of dissipation for chlorpyrifos. Chlorpyrifos degraded in sterile water with a half-life of 30 days in irradiated pH 7 aqueous solutions; the half-life in the dark controls was 74 days. No photodegradates were present at greater than 5% of the applied. The Photodegradation in Water (161-2) data requirement is fulfilled (MRID 41747206).

© Photodegradation in Soil

Based on supplemental information, it appears that chlorpyrifos on soil is degraded by processes other than photodegradation, since the half-lives of chlorpyrifos in irradiated soils were similar to the half-lives in the dark controls. The major degradate seen in the soils, TCP, was then itself photodegraded. In a photodegradation on soil study with TCP, dissipation was rapid with approximately 50% of the applied TCP degrading during the first 8 hours of sunlight exposure. The major photodegradates produced were soil-bound residues ($\leq$37.2% of applied) and carbon dioxide ($\leq$40.4% of applied). A first-order half-life of 14.1 days was calculated, however degradation appeared to be biphasic. After an initially rapid photodegradation during the first several hours, the rate of TCP degradation slowed for the remainder of the exposure period. The half-life in the dark control system was estimated at over 100 days. The Photodegradation in Soil (161-3) data requirement is fulfilled (MRID 42495403, 43509201).

(d) Photodegradation in Air

The Photodegradation in Air (161-4) data requirement is waived because chlorpyrifos has a low vapor pressure (1.87×10^{-5} mm Hg at 25°C) and low Henry's Constant (4.2×10^{-6} atm·m/mol at

25°C).

(e) Aerobic Soil Metabolism

Chlorpyrifos dissipated with a half-life of 180 days in a sandy loam soil under aerobic conditions, with the major degradate being TCP, which increased to a maximum of 32% of the applied at 365 days posttreatment. At 365 days posttreatment, volatilized [^{14}C]chlorpyrifos residues totaled 7.6% of the applied, and CO_2 totaled 13.7%. In a follow-up study, TCP resisted degradation, comprising 65.2% of the applied radioactivity after 365 days aerobic incubation. No other nonvolatile compounds were isolated from the soil, and CO_2 totaled 12.7% at the termination of the study. In another study, the half-lives of chlorpyrifos in aerobic soils ranged from 11 to 141 days in seven soils ranging in texture from loamy sand to clay, with the major degradate being CO_2, comprising 27-88% of the applied after 360 days aerobic incubation. The major non-volatile degradate formed was TCP, accounting for up to 22% of the applied ^{14}C after 360 days. Small amounts of 3,5,6-trichloro-2-methoxypyridine (TCMP; ≤8%) were also detected. Soil pHs ranged from 5.4 to 7.4 and, in general, chlorpyrifos was less persistent in soils with a higher pH. This decrease in stability with increasing soil pH was also observed in a frozen storage stability study (Robb, C.K., DowElanco Project No. 88106, 1991; no MRID). There was no obvious correlation between soil organic matter content or soil texture and the dissipation rate of chlorpyrifos. The persistence of TCP also appeared to vary among aerobic soils. The Aerobic Soil Metabolism (161-4) data requirement is fulfilled (MRID 00025619, 42144911, 42144912).

Soil persistence appears to vary over about two orders of magnitude (from a few days to well over 100 days and typically greater than 200 days for termiticidal uses) depending on soil type, environmental conditions, and possibly previous use history at the treatment site. The following table indicates differences in persistence rates in two soils which vary with application rates (initial soil concentrations from 10 to 1000 ppm) and at different temperatures and soil moisture levels (Racke *et al*., 1994).

Soil Degradation Half-lives (in months) Rates Under Different Conditions							
Application Rate (ug/L)	State	15 ºC Medium Water	15 ºC High Water	25 ºC Medium Water	25 ºC High Water	35 ºC Medium Water	35 ºC High Water
10	Texas	< 1	< 1	< 1	< 1	< 1	< 1
10	Florida	> 24	15	115	4	5	3
100	Texas	4	3	1	1	< 1	< 1
100	Florida	> 24	22	15	3	6	4
1000	Texas	6	30	10	6	2	3
1000	Florida	> 24	> 24	> 24	> 24	11	11

(f) Anaerobic Soil Metabolism

Chlorpyrifos degraded in anaerobic (flooded) loam and clay soils (half-lives of 15 and 58 days, respectively) treated with chlorpyrifos, incubated aerobically for 30 days, flooded and then kept under a nitrogen gas atmosphere. Half-lives for loam and clay soils that were incubated anaerobically (flooding plus a nitrogen gas atmosphere) for approximately 30 days and then treated with chlorpyrifos were 39 and 51 days, respectively. In both of these studies, the major degradate was TCP, which persisted under anaerobic conditions. The only other degradate identified in these studies was small amounts of 3,5,6-trichloro-2-methoxypyridine. The Anaerobic Soil Metabolism (161-5) data requirement is fulfilled (MRID 00025619).

(g) Aerobic Aquatic Metabolism

Sufficient information on the fate of chlorpyrifos exists such that aerobic aquatic metabolism data are not needed to support terrestrial uses of chlorpyrifos.

ii. Mobility

(a) Batch Equilibrium/Soil Column Leaching

Results of batch equilibrium and soil column studies show that chlorpyrifos is strongly adsorbed to most soils. Freundlich soil adsorption coefficients for soils ranging in texture from sandy loam to clay loam and in organic carbon content from 0.2 to 5.1% were 50 to 260; K_{oc}'s ranged from 3680 to 31000. Soil column leaching studies demonstrate that chlorpyrifos is relatively immobile; only 0.3 to 1.3% of the radioactivity applied to soil columns, which were eluted with 0.1 N $CaSO_4$ for 100 hours, was found in the leachate.

However, the degradate TCP is very mobile in soil. Freundlich adsorption coefficients for TCP in four soils were 0.53-1.95; K_{oc}'s ranged from 77 to 242. Results of an aged column leaching study support this, in that only 36% of the total TCP recovered was present in the 0- to 5-cm segment of the column, and 13% of the TCP recovered was present in the leachate. The Batch Equilibrium/Soil Column Leaching (163-1) data requirement is fulfilled (MRID 00155636, 00155637, 40050401, 41892801, 41892802, 42493901).

(b) Laboratory Volatility

Volatilization does not appear to be a major route of dissipation from soil for chlorpyrifos. In a laboratory volatility study, <10% of the applied chlorpyrifos volatilized after 30 days; the major volatile material was CO_2, comprising a cumulative total of 16-19% after 30 days. These results are consistent with the results of the aerobic soil metabolism studies cited above. The Laboratory Volatility (163-2) data requirement is fulfilled (MRID 41829006).

iii. Accumulation

(a) Accumulation in Fish

Chlorpyrifos bioaccumulates in aquatic organisms, but residues in tissues rapidly depurate. Chlorpyrifos bioaccumulated in rainbow trout, with maximum bioconcentration factors of 1280x in edible tissues, 3903x in non-edible tissue, and 2729x in whole fish; in general, the concentration of residues in the fish increased with exposure time. Maximum tissue concentrations were 385 ppb in edible tissues (muscle), 1174 ppb in nonedible tissues (head, skin, viscera, skeleton) and 821.5 ppb in whole fish; chlorpyrifos comprised most of the radioactivity in the fish, with the degradate 3,5,6-trichloro-2-pyridinol (TCP) and two glucuronide conjugates of TCP each comprising up to a third of the total. After 16 days of depuration, [^{14}C]residues in edible tissues, non-edible tissues, and whole fish were 5, 16, and 8 ppb, respectively. The Bioconcentration in Fish (165-4) data requirement is fulfilled (MRID 40056401).

(b) Accumulation in Oyster

Chlorpyrifos bioaccumulated in eastern oysters, with maximum mean bioconcentration factors of 1900x for whole oysters, 2500x for oyster tissues, and 87x for oyster liquor. The major degradate identified in whole oyster extracts was O,O-diethyl-O-(3,5-dichloro-6-methylthio-2-pyridyl)phosphorothioate (DMP). During depuration, total [^{14}C]residues in the whole oysters declined steadily and were $\leq$10 ppb by day 10. The Bioconcentration in Oyster (165-5) data requirement is fulfilled (MRID 42495405, 42495406).

iv. Field Dissipation

Results of field dissipation data indicate that chlorpyrifos is moderately persist under field conditions. Calculated half-lives for chlorpyrifos were 33 to 56 days in three medium-textured soils planted to field corn in California, Illinois, and Michigan. TCP persistence was roughly similar to the parent compound. The maximum accumulation of TCP occurred at the California site, with a 0.7 ppm concentration in the top 6 inches of soil at 28 days after application, compared to 1.4 ppm chlorpyrifos detected in the sample taken immediately posttreatment.

In a field study conducted in an orange grove planted on sandy, low organic matter soil, the calculated half-lives were 1.3-4, 7.3-<27, and 1.4-<32 days following the first, second, and third applications, respectively. Chlorpyrifos declined to <0.1 ppm (detection limit) by day 27 following the second treatment, and by day 32 following the third treatment; Chlorpyrifos was not detected below the 6-inch soil depth. TCP reached maximum concentrations of 0.96-1.33 ppm on days 0-1 following the third treatment and declined to <0.05 ppm by day 295.

Chlorpyrifos dissipated with initial phase (days 0-28) half-lives of 6.5-11.4 days and secondary phase (days 28-120) half-lives of 24-38.3 days when applied to fallow and turf-covered soils in Florida and Indiana. Two degradates, TCP and hydroxy-chlorpyrifos, were isolated from the treated sand soils in Florida at average maximum concentrations of 0.14 µg/g at 7 days posttreatment and 0.02 µg/g at 28 days posttreatment, respectively; TCP and hydroxy-chlorpyrifos were isolated from the treated clay loam soils in Indiana at average maximum concentrations of 1.01 at 5 days posttreatment and 0.06 µg/g at 28-56 days posttreatment, respectively. Neither chlorpyrifos nor its degradates were detected (<0.01 µg/g) below soil depths of 10-15 cm. The Terrestrial Field Dissipation (164-1) data requirement is fulfilled (MRID 40059001, 40356608, 40395201, 42874703, 42874704, 42924801, 42924802).

v. Spray Drift

No chlorpyrifos spray drift-specific studies were reviewed. Droplet size spectrum (201-1) and drift field evaluation (202-1) studies are required since the different products may be applied by aircraft and orchard airblast and due to the concern of potential risk to non-target aquatic organisms. However, to satisfy these requirements the registrant in conjunction with other registrants of other pesticide active ingredients formed the Spray Drift Task Force (SDTF). The SDTF has completed and submitted to the Agency its series of studies which are intended to characterize spray droplet drift potential due to various factors, including application methods, application equipment, meteorological conditions, crop geometry, and droplet characteristics. During 1997-98 EPA plans to evaluate these studies. In the interim and for this assessment of chlorpyrifos, the Agency is relying on previously submitted spray drift data and the open literature for off-target drift rates. The standard rates are 1% of the applied spray volume from ground applications and 5% from aerial and orchard airblast applications at 100 feet downwind. After its review of the new studies, the Agency will determine whether a reassessment is warranted of the potential risks from the application of chlorpyrifos to non-target organisms.

c. Terrestrial Exposure Assessment

At present, terrestrial wildlife risk assessment methods are limited to dietary exposures. Quantitative methodologies to assess wildlife risks from dermal absorption and inhalation exposures are not available. Since chlorpyrifos is not nearly as toxic dermally as it is orally according the results from tests on laboratory mammals, dermal exposures would not appear to be a major source of risk for terrestrial wildlife. Three types of terrestrial wildlife risk assessments are presented for chlorpyrifos. Dietary exposures for acute and chronic effects are assessed for non-granular, spray exposures. For granular exposures, terrestrial risks are assessed only for acute effects and is expressed as LD_{50}s per square foot. For spray-to-runoff applications risks are assessed as the number of standard drops per LD_{50}.

I. Non-granular Exposures and Assumptions

For pesticides applied as a non-granular product (e.g., liquids, dusts), the estimated environmental concentrations (EECs) on food items following product application are compared to LC_{50} values to assess risk. Terrestrial risk assessments are based on 0-day maximum residue levels for items as reported by Hoerger and Kenaga (1972) and modified by Fletcher *et al*. (1994). Maximum residue levels were used rather than mean levels as a conservative estimate of risk for wildlife that, by chance, might feed on foods with higher than average residue levels. This risk assessment used maximum EECs for either short grass or foliage and fruits, seeds, and large and small insects which provides a range of risk quotients depending on the particular dietary needs of a wildlife species. Measured residue levels reported in field studies on corn, citrus and golf courses sprayed with chlorpyrifos support the use of maximum residue levels for risk assessment. In case of soil incorporation following spray applications, it is assumed that soil incorporation reduces the amount of treated vegetation and seeds available to wildlife on the surface, but soil incorporation does not reduce the pesticide concentration on these food items. Soil incorporation reduces the amount of pesticide available for runoff.

The predicted 0-day maximum and mean residues of a pesticide that may be expected to occur on selected avian or mammalian food items immediately following a direct single application at 1 lb ai/A are tabulated below.

Estimated Environmental Concentrations on Avian and Mammalian Food Items (ppm) immediately following a Single Application at 1 lb ai/A		
Food Items	EEC (ppm) Predicted Maximum Residue[1]	EEC (ppm) Predicted Mean Residue[1]
Short grass	240	85
Tall grass	110	36
Broadleaf/forage plants, and small insects	135	45
Fruits, pods, seeds, and large insects	15	7

[1] Predicted maximum and mean residues are for a 1 lb ai/A application rate and are based on Hoerger and Kenaga (1972) as modified by Fletcher *et al*. (1994).

In the case of multiple applications, calculation of accumulated chlorpyrifos residue levels is complicated by the large variability of foliar dissipation half-life data. Summary of chlorpyrifos fate data (Racke 1993) show a range of foliar dissipation half-lives ranging from 0.2 days for Bermuda grass and perennial ryegrass/bluegrass in greenhouses in Michigan to 7-14 days on annual bluegrass in a field study in Ontario. In a laboratory study, Bauriedel monitored dissipation rates from foliar surfaces (unpublished data *in* Racke, 1993). Corn plants were sprayed at a rate of 1 lb/A and placed in a growth chamber held at 30^{o} C with a constant air speed of 0.8 km/hour. Chlorpyrifos dissipation during the first 24 and 48 hours posttreatment was projected as 70 and over 80 percent, respectively. Degradation rates on and in corn were gradual after Day 1, with foliar degradation half-life rates unspecified.

The pattern of chlorpyrifos dissipation appears to be biphasic. The process is described as follows: the primary mechanism of dissipation from plant surfaces has been demonstrated to be volatility. Photolysis and plant growth play secondary roles. Initial chlorpyrifos dissipation rates are rapid due to volatilization, followed by much slower dissipation rates for which half-life values have not been determined. Chlorpyrifos half-life on vegetation is conservatively assumed to be 7 days based on conclusions by Racke (1993) that most chlorpyrifos half-lives on crops are less than one week.

The Fate Model was used to calculate maximum initial EECs on terrestrial food items for multiple applications by integrating foliar degradation or dissipation rates with the number and frequency of applications. The use of maximum residues may overestimate chlorpyrifos residues in the case of multiple applications, because with each additional application, the additivity of maximum residues becomes progressively less probable. While the Fate Model is useful, the selection of maximum or mean residue levels currently remains unresolved for multiple applications, in general. While maximum initial residues were used to assess risks, it is clear that chlorpyrifos applications pose acute risks to sensitive bird and small mammal species following only one application. Additional applications simply increase the probability of more adverse effects on wildlife for a longer exposure period. In most cases, predicted maximum EECs for single applications are supported by measured chlorpyrifos residue levels reported in field studies on corn, citrus, and golf courses.

Analysis of terrestrial factors affecting chlorpyrifos residue levels indicates that the relatively short, 7-day foliar half-life of chlorpyrifos on vegetation moderates the degree of terrestrial risks from multiple applications. Based on a 7-day foliar half-life and multiple applications every seven days, Chlorpyrifos residue levels on terrestrial food items will plateau at twice the level from one application. In general, risk quotients for birds and mammals are higher for chlorpyrifos applied in a single high application than multiple applications at a lower use rate. However, multiple applications extend the time period during which non-target organisms are at risk compared to single applications.

Chlorpyrifos residues were measured in three field samples, including soils, foliage, insect and adjacent water bodies. In most cases, vegetative residue levels measured in the three chlorpyrifos field studies are similar to predicted maximum EECs from the above table following single applications. Measured residue levels from multiple applications are generally higher than residues from the first application, but the residue levels are not as great as the Fate Model predicts for multiple applications using maximum 0-day residue estimates. Comparisons of measured and predicted residue levels are presented and discussed in respective risk assessment sections for corn, citrus, and golf courses.

The validity of initial residue estimates from the nomograph are also supported by some chlorpyrifos residue data following single applications on various crops (Racke (1993). Calculation of monitored 0-day residue levels expressed as ppm for a 1 lb ai/A application are as follows. Adjusted residue levels from single applications range from 3.3 ppm on Bermuda grass in Georgia to 98 ppm soybeans foliage in Illinois. The initial residue levels on corn in Illinois ranged from 79 to 97 ppm. Comparison of measured, initial, upper levels on corn (97 ppm per lb ai/A) and soybeans (98 ppm) are within 77 percent of the nomograph estimate of the initial, upper residue limit for leafy crops (135 ppm) and for long grass (110 ppm). The reason for the reported, low residue levels on bermuda grass is unclear.

ii. Granular Exposures and Assumptions

Granular formulations pose a unique route of exposure for terrestrial wildlife. The pesticide is applied in distinct units which birds or mammals might ingest accidentally with food items or intentionally consume, as in the case of some bird species which actively seek and pick up gravel or grit to aid digestion. Granules may also be consumed by wildlife which feed on earthworms, slugs or other soft-bodied soil organisms to which the granules may adhere.

Acute risk quotients for granular formulations are calculated by dividing the maximum milligrams of chlorpyrifos granules exposed on the soil surface per square foot by LD_{50} values of various wildlife species (EPA 1992). In cases where numerous granules are applied per square foot, it may be unreasonable to assume that birds could consume the equivalent of all the granules in a square foot. Hence, an alternative method to assess potential risks is the number of granules equal to the LD_{50} value. If the number of consumed granules necessary to equal the LD_{50} is reasonable (50 granules or less), risk may be presumed. On the other hand, if 2000 granules are equivalent to the LD_{50} value, it is highly unlikely that a bird will consume that many granules. Uncertainty about risk occurs when the number of granules needed to cause toxicity effects are in a middle range of 50 to 2000 granules. In general, the smaller the number of granules required to produce an effect the greater the possibility of risk.

A major granular formulation of chlorpyrifos is Lorsban 15 G, which is a clay-based granule. DowElanco submitted information on size distribution and number of granules/gram for Lorsban 15 G. From this information, it is possible to calculate risk based on the number of granules containing the amount of pesticide equivalent to the LD_{50} values for mammals and bird species. In the corn cluster, the average granule weight and range for Lorsban 15 G was 0.064 mg (0.062-0.078) containing about 0.0096 mg ai of chlorpyrifos per granule. The average granule weight recently submitted by DowElanco is 0.075, which is within the range of weights cited in the corn cluster. The larger granule weight represents about a 17 percent higher risk to wildlife than the corn cluster risk quotients. The corn cluster values have been used in this risk assessment, in order to maintain consistency.

The following table indicates how many Lorsban/Dursban 15 G granules are equivalent to the acute LD_{50} values for select avian and mammalian species. The number of granules equivalent to the technical grade LD_{50} is equal to the LD_{50} x body weight/ mg of ai per granule.

Granular Risks to Wildlife Expressed as Number of Granules per LD_{50}
(Lorsban 15 G average weight is 0.064 mg/granule and contains 0.0096 mg ai Chlorpyrifos per granule)

Species	LD_{50} (mg/kg body wt.)	Body Weight (kg)	mg/LD_{50}	Granules/LD_{50}
House Sparrow *Passer domesticus*	10	0.0277	0.277	29
Common Grackle *Quiscalus quiscula*	5.62	0.114	0.641	67
Red-winged Blackbird *Agelaius phoeniceus*	13.1	0.0526	0.689	72
Mammal (15 grams body wt.)	97	0.015	1.455	150
Japanese Quail *Coturnix japonica*	13.3	0.178	2.367	250
Rock Dove *Columba livia*	26.9	0.100	2.690	280
Mammal (35 grams body wt.)	97	0.035	3.395	350
Common Pigeon *Columba livia*	10	0.500	5.000	520
Bobwhite Quail *Colinus virginianus*	32	0.178	5.696	590

Starling *Sturnus vulgaris*	75	0.0823	6.172	640
Ring-necked Pheasant *Phasianus colchicus*	8.41	1.135	9.545	990
Rat *Rattus norvegicus*	97	0.200	19.4	2000
Cockerel *Gallus domesticus*	34.8	1.500	52.20	5400
Mallard Duck *Anas platyrhynchos*	75.6	1.082	81.80	8500
Mammal (1000 grams body wt.)	97	1.000	97.00	10000

The small size of the granules for Lorsban 15 G reduces the probability of acute risks to some small mammals, birds and reptiles, because for many species, large numbers of granules must be eaten to cause toxic effects. But for species as sensitive as the house sparrow, consumption of relatively few granules may be needed to produce lethal effects (i.e., only 29 granules are needed to exceed its LD_{50} value). For example, if a 70 to 80-gram bird consumed eight earthworms with an average of 6 to 10 granules attached to or inside each earthworm, the exposure would be equivalent to the house sparrow LD_{50} value. Fewer granules than equivalent to the LD_{50}, may affect the most sensitive individuals within a species population. Granular equivalent to the LD_{50}s for wildlife species in the table range from 29 to 8500 granules for birds and for mammals (150 to 10,000 granules depending on body weight). Chlorpyrifos-related mortality of both birds and small mammals in field studies were reported for granular applications on corn and golf courses.

Terrestrial wildlife risk quotients for granular formulations are calculated by dividing the maximum milligrams of exposed active ingredient on the surface of an area equivalent to a square foot by the appropriate LD_{50} value times the respective animal's body weight (kg). In the case of band or T-band applications, the area is defined as the width of the band times the length of the row which equals 1 square foot. For example, if the band is 6 inches wide, the maximum exposure for a square foot area would be 6 inches by 2 feet.

Without soil incorporation, it is assumed that 100 percent of the granules remain on the soil surface and are available to birds and mammals feeding in the area. Press wheels push granules flat with the surface of the ground, but do not incorporate granules into the soil. If granules are incorporated into the soil during band and T-band applications or after broadcast applications, it is assumed that only 15 percent of the applied granules remain available to wildlife. It is assumed that only 1 percent of the granules are available on the soil surface following in-furrow applications.

Listed below are the formulae used for calculating risk quotients for different granular application methods.

Granular Broadcast (no soil incorporation):

Risk Quotient = $\underline{\text{lb ai/A X 453,590 mg/lb X 1 ft}^2\text{ foraging area}}$

$$\frac{}{43{,}560\ ft^2/A\ [LD50\ (mg\ ai/kg\ body\ wt.)\ \times\ body\ wt\ (kg)]}$$

Granular Broadcast (soil incorporated):

$$\text{Risk Quotient} = \frac{lb\ ai/A\ \times\ 453{,}590\ mg/lb\ \times\ 0.15\ exposed\ \times\ 1\ ft^2\ foraging\ area}{43{,}560\ ft^2/A\ [LD50\ (mg\ ai/kg\ body\ wt.)\ \times\ body\ wt\ (kg)]}$$

Granular Band and T-band Treatments (Unincorporated):

$$\text{Risk Quotient} = \frac{(oz\ ai/1000\ ft\ row)\ \times\ 1000\ ft\ row\ \times\ 28{,}349\ mg/oz\ \times\ 1\ ft^2\ foraging\ area}{band\ width\ (ft.)\ \times\ LD50\ \times\ body\ wt.\ (kg)}$$

Granular Band and T-band Treatments (Soil Incorporated):

Risk Quotient =

$$\frac{(oz\ ai/1000\ ft\ row)\ \times\ 1000\ ft\ row\ \times\ 28{,}349\ mg/oz\ \times\ 0.15\ exposed\ \times\ 1\ ft^2\ foraging\ area}{band\ width\ (ft)\ \times\ LD50\ (mg/kg\ body\ wt.)\ \times\ body\ wt.\ (kg)}$$

Granular In-furrow Treatments:

Risk Quotient =

$$\frac{(oz\ ai/1000\ ft\ row)\ \times\ 1000\ ft\ row\ \times\ 28{,}349\ mg/oz\ \times\ 0.01\ exposed\ \times\ 1\ ft^2\ foraging\ area}{LD50\ (mg/kg\ body\ weight)\ \times\ body\ weight\ (kg)}$$

d. Water Resource Assessment

Chlorpyrifos is not currently regulated under the Safe Drinking Water Act (SDWA). Therefore no MCL has been established for it and water supply systems are not required to sample and analyze for it. It has one-day and 10 day HALs of 30 µg/L, and a lifetime HAL of 20 µg/L. The limited data EFED has on chlorpyrifos in surface water as well as summaries from the NAWQA program suggests that it is probably unlikely that the annual average concentrations of chlorpyrifos will exceed the lifetime health advisory or that peak or short term average concentrations will exceed the 1-10 day health advisory in the actual surface water sources for drinking water. Furthermore, the intermediate to high soil/water partitioning of chlorpyrifos should limit somewhat its loading to surface water and make the primary treatment processes employed by most surface water source supply systems effective in removing it. However, the HED LOC for drinking water is much closer to 1 ug/L than the 20ug/L to 30 ug/L HALs. There is also concern over the possibility that the effects of chlorpyrifos may be additive along with other cholinesterase inhibitors such as other organophosphates and/or some of their degradates.

HAL's have not been established for the major degradates, TCP and 2-methoxy-3,5,6-trichloropyridine. However, even though the toxicity of TCP is low compared to chlorpyrifos, the persistence and mobility of TCP suggests that it may be of concern in drinking water. TCP is also the major degradate of the herbicide, triclopyr.

I. Surface Water Fate and Exposure Assessment

Chlorpyrifos is moderately to highly persistent in the environment and binds to soil. Chlorpyrifos can contaminate surface water at application via spray drift and can be transported offsite on sediment borne by runoff. It has been shown that chlorpyrifos will leave corn watersheds in Illinois and can be transported to ponds a short distance from the fields; quantities of chlorpyrifos transported are generally less than 1% of the applied (00144906), but the quantities transported of its major degradate (TCP) may be greater. Substantial fractions of applied chlorpyrifos could be available for runoff for several weeks to months post-application (aerobic soil metabolism half-lives of 11-180 days for 8 soils; terrestrial field dissipation half-lives of 33-56 days). The intermediate to high soil/water partitioning of chlorpyrifos (K_{oc}s of 3680-31,000; SCS/ARS database K_{oc} of 6070; K_ds of 50-260) indicate that most of chlorpyrifos runoff is generally via adsorption to eroding soil rather than by dissolution in runoff water. However, in some cases within the lower ranges of adsorption and when runoff volume greatly exceeds sediment yield, dissolution in runoff water may also contribute significantly to runoff.

The relatively low to moderate susceptibility of chlorpyrifos to hydrolysis (half-lives of 72 days at pHs 5 and 7 and 16 days at pH 9), direct aqueous photolysis (half-life of 30 days in sunlight), low volatilization (intermediate Henry's Law constant = 4.2×10^{-6} atm*m^3/mol), and degradation under aerobic conditions indicate that chlorpyrifos will be somewhat persistent in the water columns of some aqueous systems that have relatively long hydrological residence times. However, volatilization and/or adsorption to sediment may substantially reduce the persistence of dissolved chlorpyrifos in shallow waters and in waters receiving influxes of uncontaminated sediment, respectively. In his comprehensive literature review, Racke (1993) attributed short dissipation half-lives in the water column (sometimes < 1 day) to volatilization and/or adsorption to sediment. The relatively low to moderate susceptibility of chlorpyrifos to degradation under anaerobic conditions indicates that it will also be somewhat persistent in anaerobic bottom sediment.

The intermediate to high soil/water partitioning of chlorpyrifos indicates that its concentration in sediment will be much greater than its concentration in water. BCFs greater than 1000X in the rainbow trout exposed to 0.30 ppb in a 28-day flow-through study (1280X for edible tissues, 2727X for whole fish, and 3903X for viscera) and in eastern oysters (2500X for edible tissues, 3900X for viscera, and 1900X for whole body) indicate some potential for bioaccumulation. Although, the observed rapid depuration rates should somewhat modify its bioaccumulation potential, chlorpyrifos has been detected at several ppb in the tissues of many fish collected from many different surface waters.

As part of the National Study of Chemical Residues in Fish (US EPA, 1992), fish were collected from 362 sites nationwide, and analyzed for chlorpyrifos. Approximately 23% of the samples collected had chlorpyrifos residues above the detection limit of approximately 0.05 µg/kg. The maximum value was 344 µg/kg in carp tissue collected from the Alamo River in CA. Concentrations between 60 and 70 µg/kg were detected in fish collected from GA, TX, WI, and CA. The cumulative frequency curve for chlorpyrifos in fish tissue is attached. The 90th percentile value is slightly greater than 10 µg/kg. Since chlorpyrifos was found to rapidly depurate in the fish BCF test, the presence of chlorpyrifos residues in fish would suggest existing or recent exposures.

The major degradate of chlorpyrifos in the environment under most conditions is 3,5,6-trichloro-2-pyridinol (TCP). TCP appears to be more persistent than chlorpyrifos (substantial amounts remain 365 days post-application) and it exhibits much lower soil/water partitioning (K_ds of 0.53-1.95) than chlorpyrifos. Consequently, substantial amounts of TCP are probably available for runoff for longer periods than chlorpyrifos and TCP is probably more persistent in water/sediment systems than chlorpyrifos. The relatively low soil/water partitioning of TCP indicates that its concentrations in sediment and water are probably comparable and that runoff occurs primarily by dissolution in runoff water rather than by adsorption to eroding soil. The low soil/water partitioning of TCP suggests that its bioaccumulation potential is probably low.

There are two particularly important issues with regard to chlorpyrifos use as a termiticide that greatly affect the degree to which the parent compound impacts water resources and potentially impacts drinking water quality. First, termiticide use rates are much higher than any other chlorpyrifos use and the application method around dwellings include much deeper soil incorporation than for agricultural uses. Second, soil persistence, which appears to vary over about two orders of magnitude (from a few days to well over 100 days and typically greater than 200 days for termiticidal uses) depending on soil type, environmental conditions, and possibly previous use history at the treatment site. Issues regarding the degradate, TCP, are discussed further below. While the impacts of the termiticidal uses of chlorpyrifos on water resources are more localized than for other uses, the impacts are also potentially much more intense. Therefore, the termiticidal use is discussed separately in the Drinking Water Assessment section.

For **aquatic risk assessments**, EFED used the GENEEC for most uses. The PRZM2.3-EXAMS Models was used to generate Tier 2 (single site over multiple years) EECs for Chlorpyrifos in a 1-hectare surface area, 2-meter deep pond draining 10 hectares of Iowa, Georgia, and Mississippi corn fields and 10 hectares of Georgia peanut, Mississippi cotton, North Carolina tobacco, and Florida citrus fields. The EECs were generated to use in performing aquatic risk assessments. The non-corn and Mississippi corn scenarios were reasonable high exposure scenarios. The Iowa corn scenario was more typical of use on corn than the Mississippi corn scenario. Each scenario was simulated over 36 years. One in 10 year peak and 96-hour, 21-day, 60 day, and 90-day EECs for each scenario are summarized in the table below. The EECs range from a 90-day average of 0.7 ppb for the Iowa corn scenario to a peak 40.6 ppb for the North Carolina tobacco scenario. The modeling report should be consulted for more details and the cumulative frequency graphs (see Appendix IV). The GENEEC model was use to estimate EECs for other crops and uses. The following chemical and fate data for chlorpyrifos were used for input into the GENEEC, PRZM2.3-EXAMS and SCI-GROW Models.

Summary of Selected Environmental Fate Properties for Chlorpyrifos			
Property	Range (mean or median)	Value used in Assessment	Model(s)
Solubility	2.0 mg/L (ppm)	2.0 mg/L (ppm)	GENEEC, PRZM-EXAMS
Hydrolysis	pH 5: 72 days pH 7: 72 days pH 9: 16 days	72 days	GENEEC, PRZM-EXAMS
Photolysis	30 days @ pH 7	29.6	GENEEC, PRZM-EXAMS
Aerobic Soil Metabolism $T_{1/2}$	11 to 180 days (mean = 63 days)[1]	180 days 76.9 days 63 days	GENEEC PRZM-EXAMS SCI-GROW
Aerobic soil Metabolism for **Termiticide Rates**	175 to 1576 days (mean = 506 days) (median = 230 days)[2]	506 days	SCI-GROW
Field Dissipation $T_{1/2}$ (supporting information only)	1 to 56 days at 6 sites (mean = 27 days)[3]	not directly used	not directly used
Anaerobic Soil Metabolism T1/2	39 to 51 days (2 soils)	not considered	
Aerobic Aquatic Metabolism $T_{1/2}$	no data	0 days	
Kads	50 to 260	not used	
KOC	360 to 31000	6070	GENEEC, PRZM-EXAMS, SCI-GROW

1 The range of soil half-lives in a 1979 study with undisturbed samples from seven different soils was 11 to 141 days. The mean and median soil half-lives were 63 and 34 days, respectively. A 180-day half-life was measured in a subsequent study of metabolism in one soil.

2 Racke, K. D., D. D. Fontaine, R. N. Yoder and J. R. Miller 1994. Chlorpyrifos degradation in soil at termiticidal application rates. Pesticide Sci. 42:43-51. This published study was conducted by DowElanco, the registrant.

3 Field dissipation half-lives or 50 % disappearance times in 3 sets of studies were:
- 33, 46, and 56 days (3 sites);
- 1.3 to ca. 15 days (3 applications at 1 citrus site), data too variable to estimate precisely; and
- 6 to 11 days at 2 sites with fallow and turf applications (longer secondary "half-lives")

The following chemical and fate data were used for input into the GENEEC and or SCI-GROW model for 3, 5, 6-trichloro-2-pyridinol.

Summary of Selected Environmental Fate Properties for 3,5,6-Trichloro-2-pyridinol			
Property	Range (mean or median)	Value used in Assessment	Model
Solubility	117 mg/L (ppm) at pH 2.5, increases at higher pH	500 mg/L (ppm)	GENEEC
Hydrolysis	pH 5: >> 30 days[1] pH 7: >> 30 days pH 9: >> 30 days	180 days	GENEEC, SCI-GROW
Photolysis	0.33 days (soil) 2 @ pH 7	1 day	GENEEC, SCI-GROW
Aerobic Soil Metabolism $T_{1/2}$	600 days est. range 65 to >360 in parent studies[2]	600 days	GENEEC, SCI-GROW
Aerobic Soil Metabolism for **Termiticide Rates**	>> 24 months in each of 5 soils	1500 days	SCI-GROW
Anaerobic Soil Metabolism $T_{1/2}$	>500 and >1500 days (2 soils)[3]	not considered	GENEEC

Summary of Selected Environmental Fate Properties for 3,5,6-Trichloro-2-pyridinol			
Aerobic Aquatic Metabolism $T_{1/2}$	no data	0 days	
K_{ads}	0.53 to 1.95 ml/g; 0.3 to 20.3 ml/g in previous study[4]	not used	
K_{oc}	77 to 242 (136, geometric mean); 27 to 389 (168 mean) in previous study[3]	136	GENEEC, SCI-GROW

[1] TCP accumulated without apparent degradation over the 30-day study period at each pH.

[2] In 7 soils, aerobic soil half-lives estimated to be (soil series name in parenthesis):

65 days (Miami) 220 days (Barnes)
70 days (Commerce) 220 days (Catlin)
90 days (German) 360 days (Norfolk)
360 days (Stockton)

These estimates are from the aerobic metabolism studies with Chlorpyrifos parent applied.

[3] Racke, K. D. and S. T. Robbins. 1991. Factors affecting the degradation of 3, 5, 6-trichloro-2-pyridinol in soil. Amer. Chem. Soc. Symposium Series No. 459, pp. 93-107.

[4] Twenty-five soils were tested in this study, however, desorption coefficients were not determined.

In the following table, estimated environmental concentrations (EECs) for chlorpyrifos are presented for a typical, one-acre farm pond for select uses on some major crops treated with chlorpyrifos. The PRZM2.3/EXAMS and GENEEC Models were used to calculate the pond EECs. Only eight chlorpyrifos uses were assessed using the PRZM2.3-EXAMS Model: corn (4 scenarios) and one scenario each for citrus, peanuts, cotton, and tobacco. All other aquatic assessments for chlorpyrifos uses were made using the GENEEC Model.

Estimated Environmental Concentrations For Aquatic Exposure With PRZM-EXAMS & GENEEC

Site	Application Method	Appl. Rate (lbs ai /A)	Initial (PEAK) EEC (ppb)	4-Day average EEC (ppb)	21-day average EEC (ppb)	60-day average EEC (ppb)	90-day average EEC (ppb)
Corn - Iowa (PRZM-EXAMS) Marshall Silty Clay Loam	1 ground spray appl., incorp.2"	3	11.1	8.7	4.5	2.7	1.9
Corn - foliar spray (GENEEC)	1 ground spray, unincorporated	1.5	5.5	4.8	2.7	---	---
Corn - foliar spray (GENEEC)	1 aerial appl.	1.5	7.7	6.8	3.8	2.3	---
Corn - foliar spray (GENEEC)	3 aerial appl. 14-day interval	1.5	24	21.5	11.7	6.8	---
Corn - GA spray (PRZM-EXAMS) Cowarts Sandy Loam	11 aerial, foliar appl.	1	15.8	12.8	7.4	5.6	4.3
Corn - granular, pre-plant (GENEEC)	1 ground appl., incorporated 4"	2	1.66	1.44	0.81	0.51	---
Corn - granular, pre-plant, Iowa (PRZM-EXAMS - Corn Cluster)	1 typical ground appl.,incorp. 4"	1.3	4.0	3.1	1.6	1.0	0.7
Corn - granular, pre-plant, Miss. (PRZM-EXAMS - Corn Cluster)	1 typical ground appl., incorporated 4"	1.3	4.6	3.7	1.9	1.1	0.7
Corn - granular, post-plant, (GENEEC)	1 ground appl. 7" T Band, 1" incorp.	2.4 oz./1000 ft. of row	8.63	7.48	4.2	2.6	---

Estimated Environmental Concentrations For Aquatic Exposure With PRZM-EXAMS & GENEEC

Site	Application Method	Appl. Rate (lbs ai /A)	Initial (PEAK) EEC (ppb)	4-Day average EEC (ppb)	21-day average EEC (ppb)	60-day average EEC (ppb)	90-day average EEC (ppb)
Corn - granular, foliar, (GENEEC)	2 aerial appl. 14-day interval	0.975	6.35	5.5	3.1	1.9	---
Citrus - Florida (PRZM-EXAMS) Adamsville Sand	2 airblast appl., 30-day interval	3.5	27.6	21.4	11.8	8.3	6.7
Peanuts - Georgia PRZM-EXAMS Tifton Loamy Sand	2 ground spray, pre/post-plant 40-day interval	2	15.4	11.5	6.0	3.6	2.7
Cotton - Miss. (PRZM-EXAMS) Loring Silt Loam	6 aerial, foliar spray appl.	1	14	10.8	5.7	3.7	3.0
Tobacco - NC (PRZM-EXAMS) Norfolk Loamy Sand	1 pre-plant, ground spray	5	40.6	31	14.7	7.7	5.4

The above model-based EECs for a pond are in the range of 0.7 to 40 ppb for chlorpyrifos, whereas the available monitoring data for flowing waters are in the ppt range. Because of the relatively high soil/water partitioning of chlorpyrifos, EFED does not believe that the differences between the estimated EECs and monitoring data are due to any over predictions of pesticide loadings to surface water which have been observed for pesticides with low soil/water partitioning. The model generated EECs are generated for high exposure agricultural scenarios and represent one in ten-year EECs in a one-acre farm pond or other similar water body with no outlet that receives pesticide loading from an adjacent 100% cropped, 100% treated field. As such, the computer generated EECs represent screening levels for most surface waters even if they approximate upper bound concentrations that might be seen in actual edge of the field pond.

The EECs generated by the PRZM/EXAMS and GENEEC models are used for assessing the acute and chronic risks for freshwater and estuarine organisms in ponds and estuarine areas. Chlorpyrifos concentrations reported in NAWQA and California monitoring data was used to assess risks for some typical flowing waters. Acute aquatic risk quotients were calculated using the peak EECs. For reproductive effects, it is unclear what duration of exposure would be necessary to produce the chronic toxic effects observed in laboratory tests. Baird *et al*. (1991) demonstrated that the daphnid reproductive MATC value following a 48-hour exposure was equivalent to the MATC for a 21-day study for 3,4-dichloroaniline. In the case of the fathead minnow full life cycle, the most sensitive endpoint was mortality which was observed in both F_0 fry and F_1 offspring when the fry were only 25 days old. Since fry mortality, the most sensitive endpoint, occurred when the fry were 25 days old, the appropriate, longer exposure period for fish reproduction effects would be closer to the 21-day EEC than the 56- or 60-day EEC. In order to address uncertainties about the exposure duration period necessary to produce the observed reproductive effects for fish and invertebrates, the chronic risk quotients were calculated using an exposure period ranging from 96-hour to 21-day EECs. In most cases, aquatic risk quotients for reproductive effects exceed levels of concern irrespective of which EEC time period was selected. The shortest half-life in water for chlorpyrifos is 29.6 days. EECs used in the estuarine risk assessments are the same as those calculated for the farm pond, because some estuaries may be similar to farm ponds in which pesticides and sediments are readily deposited and from which little is transported out of the system. An estuary differs from a farm pond in that the estuary usually has tidal action that may flush residues back and forth with each tide and may eventually disperse pesticides throughout the system.

While the EECs are modelled for a 2-meter deep pond, other types of aquatic habitats may border treatment areas. Many shallow water areas less than 2 meters deep are biologically important. Bluegill, the fish species found to be most sensitive to chlorpyrifos, lives and reproduces in water 1 meter deep or less. Dramatic declines in amphibian populations have been reported nationwide. There is no direct evidence to show that chlorpyrifos is responsible for the decline in amphibian populations. However, in the case of chlorpyrifos, the tadpole stage of some toads is as sensitive as bluegills and the field studies reported chlorpyrifos-related deaths of an adult frog and toad. Many amphibians live and reproduce in shallow water 1/6 meter deep, including temporary puddles. For chlorpyrifos, the EECs and risk quotients would increase somewhat for organisms inhabiting shallow waters compared to aquatic species in a 2-meter pond.

In cases where multiple applications on a crop differ, the GENEEC aquatic risk quotients could be lower or greater than the values cited in the Risk Quotient tables. The GENEEC Model was used to calculate EECs for most uses. In those cases where application methods differ from one application to the next, the GENEEC Model can not integrate use differences, such as variable application intervals, different use rates or various application methods. For each particular use method, risk quotients for multiple applications were calculated, but risk quotients were not determined when multiple applications were different. For example, the preplant application to corn is soil incorporated, while the other applications (3 or 4) are broadcast at irregular intervals (i.e., post-emergence, tassel, and/or whorl) using spray and/or granular applications. In the case where crops have ground cover, aquatic risks may be lower, because the GENEEC Model does not differentiate EECs for application sites were erosion may be reduced by a cover crop, grass, or ground vegetation. The aquatic risk quotients for pome fruits and nut crops are likely to be overestimated, because these orchard floors may be mowed and a ground cover exists to some extent. This contrasts with citrus groves in some areas where the soil is normally disked to prevent growth of weeds. The PRZM3-EXAMS Model can integrate the complexities of multiple applications, such as different application methods, different use rates, and variations in retreatment intervals.

Although, runoff events and aquatic exposures are highly variable and episodic, measured chlorpyrifos concentrations in water samples were found which exceed levels toxic to aquatic organisms in all three field studies. The size and depth of aquatic habitats where chlorpyrifos residues were found have generally not been reported. In the case of the corn field spray study, mean chlorpyrifos levels measured in adjacent water bodies ranged from non-detect to 66.9 ppb; the highest measured water concentration was 115 ppb which was collected 7 days after treatment. In the corn field study with granular treatments, measured water samples ranged from non-detect to 1.8 ppb. In the California citrus field study, mean measured water samples ranged from non-detect to 244 ppb; the highest water sample measured 486 ppb. One or more water samples in both the corn and citrus studies exceed the corresponding modelled EECs used for risk assessment. In the golf course study, measureable chlorpyrifos levels were found in water on Day 0 at the two granular treatment sites (i.e., 1.69 and 2.5 ppb); no measureable levels (detection limit 1.0 ppb in water) were found in aquatic habitats adjacent to sprayed golf course sites. In the corn and citrus field studies, the highest water measurements were two and three orders of magnitude higher than fish and aquatic invertebrate LC_{50} values, respectively. In the golf course study, chlorpyrifos were about 1 to 2 orders of magnitude higher than fish and aquatic invertebrate LC_{50} values, respectively. Fish kills were reported in aquatic habitats adjacent to treated areas in both the citrus and golf course studies. Dead fish, water and soil samples were sent to the sponsor for analyses; no information on these samples have been received by the Agency. Comparison of EECs with measured levels are presented under the risk discussions for each crop.

ii. Analytical Monitoring Studies in Surface Waters

The monitoring data represent flowing water receiving pesticide loadings from partially cropped, partially treated watersheds much of which is not adjacent to the water body. Therefore, such data may more accurately represent exposure of aquatic organisms to chlorpyrifos in the flowing water of actual watersheds than the computer estimated EECs for a one-acre farm pond. However, the data are derived from multiple pesticide USGS studies. Although there is substantial overlap between a number of USGS stations and chlorpyrifos use sites, sampling sites do not necessarily represent watersheds where chlorpyrifos is most heavily used. Therefore they may reflect less exposure to chlorpyrifos than in watersheds where it is heavily used. Also, chlorpyrifos concentrations in lakes and ponds both adjacent and not adjacent to treated fields may sometimes be substantially greater than in flowing water. In the citrus field study, two water samples collected on Day 1 tested positive for chlorpyrifos. The measured concentrations in these two water samples were 1.2 and 486 ppb, which clearly bracket all the above, modeled EECs. However, it is unclear how persistent or pervasive chlorpyrifos residues were or the size of the water bodies from which the samples were collected.

A number of surface water monitoring studies are available on chlorpyrifos, mostly on flowing waters, as opposed to the farm pond scenario modelled by the GENEEC and PRZM2.3/ EXAMS Models. Some early monitoring studies prior to 1990 did not detect chlorpyrifos at the limits of detection (i.e., 0.05-0.1 ppb) in heavy pesticide use areas in Iowa and Illinois. The following table summarizes the results of major surface water monitoring studies for chlorpyrifos parent (residues are explicitly stated to be, or appear to be, for dissolved residues in these studies).

Chlorpyrifos Concentrations Found in Major Surface Water Monitoring Studies					
Study Identification	Location, type of water	Number of samples or sites	Detection limit, ug/L	% Detections	Highest Detection
Wnuk et al. (1987)	Iowa, community water supply systems	35 sites	0.1	0.0	<0.1

Moyer and Cross (1990)	Illinois	30 sites	0.05	0.0	<0.05
Goolsby and Battaglin (1993)	Mississippi River basin rivers and streams	381 samples, 8 sites	0.005	3.1	0.2
Kimbrough and Litke (1995)	two Colorado watersheds	50 samples, 2 watersheds	0.008	12.0	0.08
MacCoy et al. (1995) (samples collected every day or two from one location)	San Joaquin River, CA	~200 samples, 1 location	0.012	~6	0.04
Gilliom et al. (1997, USGS web site)	20 NAWQA study units all over U.S.: agricultural streams	1530 samples, 37 streams	0.010	14.6	0.40
Gilliom et al. (1997, USGS web site)	20 NAWQA study units all over U.S.: urban streams	604 samples, 11 streams	0.010	26.5	0.19
Gilliom et al. (1997, USGS web site)	20 NAWQA study units all over U.S.: mixed-land use large streams	555 samples, 14 streams	0.010	14.4	0.13
Hippe et al. (1994, USGS Report 94-4183)	Apalachicola-Chattahoochee-Flint Rivers, GA, AL, FL	57 weekly samples, Urban watershed	~0.005	65.0	0.051
Crawford et al. (1995, USGS Fact Sheet 233-95, USGS web site, and personal communication)	White River Basin, southern Indiana.	585 samples, 6 streams and rivers	0.004	27.7	0.130
Thurman et al. (1998, USGS Fact sheet FS-022-98)	Mississippi delta: cotton production areas of LA, MS, AR, TN, KY, & MO.	64 sites in streams and rivers	0.010	2	0.2

Dissolved Chlorpyrifos Concentrations Distributions in Large-Scale Surface Water Monitoring Studies

Study Identification	Location, type of water	Number of samples or sites	Detection limit, ug/L	% Detections	90th Percentile Detection	95th Percentile Detection	Highest Detection
Gilliom et al. (1997, USGS web site)	20 NAWQA study units all over U.S.: agricultural streams	1530 samples, 37 streams	0.010	14.6	0.017	0.031	0.400

Dissolved Chlorpyrifos Concentrations Distributions in Large-Scale Surface Water Monitoring Studies							
Gilliom et al. (1997, USGS web site)	20 NAWQA study units all over U.S.: urban streams	604 samples, 11 streams	0.010	26.5	0.020	0.038	0.190
Gilliom et al. (1997, USGS web site)	20 NAWQA study units all over U.S.: mixed-land use large streams	555 samples, 14 streams	0.010	14.4	0.012	0.020	0.130
Crawford et al. (1995, USGS Fact Sheet 233-95, USGS web site, and personal communication)	White River Basin, southern Indiana. Data collected from 1992 to 1996.	585 samples, 6 streams and rivers	0.004	~14	0.016	0.025	0.130

In two studies conducted prior to 1990, chlorpyrifos was not detected at detection limits in the 0.05-0.1 ppb range. The State of Iowa (Wnuk, et al 1987) analyzed for chlorpyrifos in one raw and one finished water sample collected from each of 35 Iowa surface water supply systems. The samples were collected during the first runoff event occurring between May 1 and July 1 1986. Chlorpyrifos was not detected in any of the filtered samples above a detection limit of 0.1 µg/L. The State of Illinois (Moyer and Cross 1990) sampled 30 surface water sites for pesticides at various times from October 1985 through October 1988. Although substantial use in Illinois was a criterion for pesticides being included in the analyses, total chlorpyrifos was not detected in any of the samples at or above the detection limit of 0.05 µg/L.

More recent studies in three different areas of the country using lower detection have reported chlorpyrifos concentrations in filtered surface water samples in the several pptr range, but generally less than 200 pptr (0.2 ppb or 0.2 µg/L). The USGS (Goolsby and Battaglin 1993) sampled 8 widely spread locations in 3 rivers and 5 tributaries within the Mississippi Basin at frequent intervals from April 1991 to April 1992. A minimum total of 381 samples were collected from the 8 sampling locations. Chlorpyrifos was detected at dissolved concentrations between a reporting limit of 0.005 µg/L and a maximum of approximately 0.2 µg/L in 12 samples collected from 6 of the 8 sampling locations. The USGS (Kimbrough and Litke 1995) collected samples from each of two Colorado watersheds at least monthly from April 1993 through March 1994. Samples were collected more frequently in late spring and early summer. A total of 25 samples were collected from each watershed. Chlorpyrifos was detected above a method detection limit of 0.008 µg/L in 6 of the samples collected from an agricultural watershed with concentrations ranging from 0.01 µg/L to 0.22 µg/L. Chlorpyrifos was detected in 9 of the samples collected from a primarily urban watershed at concentrations ranging from 0.006 µg/L to 0.084 µg/L. The USGS (MacCoy, Crepeau, and Kuivila 1995) collected samples daily or every other day from the San Joaquin River at Vernalis, California from October 1992 through September 1993. Chlorpyrifos was detected in 13 samples at concentrations all below the reported method detection limit of 0.044 µg/L. Reported concentrations ranged from 0.012 to 0.043 µg/L.

As part of the National Water Quality Assessment (NAWQA) program, the USGS sampled the flowing waters of 20 major watersheds (study units) in the early to mid 90s and analyzed the samples for up to 85 pesticides and metabolites including chlorpyrifos. Given the widespread distribution of chlorpyrifos use and the USGS study units, there was substantial overlap between the study units and chlorpyrifos use.

The USGS has statistically summarized (for the first 20 NAWQA study units) filtered sample (e.g., dissolved) chlorpyrifos concentrations for 37 streams, 11 streams, and 14 streams draining predominately agricultural, urban, and mixed agricultural/urban watersheds, respectively (//water.wr.usgs.gov/pnsp/gwsw1.html).

Of the 1530 samples collected from the 37 agricultural streams, 14.6% and 3.01% had dissolved chlorpyrifos concentration > 0.01 ug/L and > 0.05 ug/L, respectively. The 50th percentile, 90th percentile, 95th percentile, and maximum dissolved chlorpyrifos concentrations reported across the 37 agricultural streams were < MDL of 0.003 ug/L, 0.017 ug/L, 0.031 ug/L, and 0.40 ug/L, respectively.

Of the 604 samples collected from the 11 urban streams, 26.5% and 3.31% had dissolved chlorpyrifos concentration > 0.01 ug/L and > 0.05 ug/L, respectively. The 50th percentile, 90th percentile, 95th percentile, and maximum dissolved chlorpyrifos concentrations reported across the 11 urban streams were < MDL of 0.003 ug/L, 0.02 ug/L, 0.038 ug/L, and 0.34 ug/L, respectively. Somewhat surprisingly, the distribution of chlorpyrifos concentrations across the 11 urban streams is similar to the distribution across the 37 agricultural streams.

Of the 555 samples collected from the 14 large agricultural/urban streams, 14.4% and 1.98% had dissolved chlorpyrifos concentration > 0.01 ug/L and > 0.05 ug/L, respectively. The 50th percentile, 90th percentile, 95th percentile, and maximum dissolved chlorpyrifos concentrations reported across the 14 agricultural/urban streams were < MDL of 0.003 ug/L, 0.012 ug/L, 0.020 ug/L, and 0.13 ug/L, respectively.

iii. Biomonitoring in Surface Waters

A number of biomonitoring studies have identified chlorpyrifos as a problem in several areas around the country. In some areas chlorpyrifos levels have tested toxic to *Ceriodaphnia* in rainfall, POTW discharges, storm drain systems, and river segments in agricultural areas. Nationwide pesticide monitoring studies indicate widespread Chlorpyrifos residues in fish samples.

Bioassay of rainfall samples in Sacramento and San Francisco area show chlorpyrifos residue levels which are toxic to *Ceriodaphnia dubia*, the invertebrate component of EPA's three species bioassay test.

Recent bioassay monitoring in the San Francisco Bay area has detected chlorpyrifos and diazinon in discharges from both sewage treatment plants (POTWs) and municipal storm drain systems that are toxic to whole effluent test organisms. Aquatic toxicity of these two organophosphate pesticides show additive toxicity. In addition, some toxicity identification evaluations conducted by dischargers, state agencies, and USEPA Environmental Research Laboratory in Duluth, have identified one or both of these pesticides as toxicants in urban discharges toxic to test organisms in Arizona, Kentucky, Nevada, and Texas. Although these discharges are generally substantially diluted by receiving water, such toxic discharges containing chlorpyrifos often exceed NPDS permit levels and appear to be widespread.

Invertebrate bioassays of receiving water in aquatic habitats areas adjacent to agricultural areas in the San Joaquin Basin show chlorpyrifos and diazinon toxicity. During a two and a half year bioassay study between 1988 and 1990, a 43-mile reach of the San Joaquin River between the confluence of the Merced and Stanislaus Rivers has tested toxic to *Ceriodaphnia dubia* about 50 percent of the time. The investigators conclude that the toxicity appears to be caused by pesticides in storm and tailwater runoff from row and orchard crops. Chlorpyrifos was identified more often than any other pesticide as the source of toxicity. The authors determined that there are two seasonal, peak toxicity periods: January-March and April-June. The seasonal peak between January and March occurs during the rainy season and follows dormant spray applications on stone fruits, apple, pear and almond orchards between December and February. The seasonal chlorpyrifos peak between April and June results from irrigation of alfalfa and sugar beets treated in March to April. Irrigation begins in April. The water flows across the fields in furrows to creeks or collection canals which empty into the river. Irrigation water is flushed from the field in order to prevent toxic salt build-up in the soils. The tailwater is believed to be the primary vehicle responsible for transporting pesticides into surface water (Foe 1995).

A nationwide monitoring study (US EPA 1992) indicates the presence of chlorpyrifos in approximately 23 percent of the samples of fish from 314 sites. The number of fish with chlorpyrifos residues demonstrate extensive off-field movement and exposure of chlorpyrifos to aquatic organisms. Fish and other aquatic organisms may bioaccumulate chlorpyrifos residues from the water, sediments, and/or their food. Chlorpyrifos residues in aquatic organisms are a route of exposure for birds and mammals, which feed on these aquatic organisms. Some piscivorus, like egrets, herons, kingfishers, pelicans, cormorants, water snakes and turtles may swallow a fish whole. Other piscivorus species, like mink, river otter, osprey, bald eagle, gulls and terns may feed largely on the viscera which may have higher pesticide residue levels.

Assessment of risks for mammals and birds feeding on aquatic organisms in chlorpyrifos-contaminated habitats is limited to bioconcentration (i.e., residue uptake from water only). It does not address bioaccumulation of pesticide residues (i.e., residue uptake from sediments and in their diet). In aquatic habitats, some pesticides are taken up by organisms directly from the water and sediments. Predators on these organisms also accumulate pesticides in their diet. While the residues bioaccumulated from food may increase exposure levels higher than bioconcentration from water alone, aquatic organisms usually obtain the largest proportion of their pesticide residues directly from the water via absorption through the gills. Since aquatic bioaccumulation data are unavailable for uptake of chlorpyrifos from sediments and food by prey species, the assessment of risks to piscivorus is limited to exposures based on BCF values and underestimates the risks, if any, to piscivorous mammals and birds.

Gross estimates of the dietary exposures for piscivorous mammals and birds can be made by multiplying the average water concentration for the time it takes to reach steady-state in the bioconcentration test times the bioconcentration factor (BCF). Chlorpyrifos residue levels in fish were estimated by multiplying the 21-day EEC from GENEEC model times the BCF values for whole fish (2730X) and viscera (3900X). Assessment of risks to piscivorus were estimated by comparing the estimated residue levels in fish to the subacute dietary LC_{50} and reproductive NOEC values for mammals and birds. Risk quotients have not been used for risk assessment of piscivorus, because the LOC criteria have not been evaluated for this risk scenario.

iv. Ground Water Assessment

Based on information from environmental fate studies, chlorpyrifos is unlikely to leach to ground water in measurable quantities from most typical use scenarios. In two terrestrial field dissipation studies (**40059001** and **40395201**), chlorpyrifos was not detected at soil depths greater than 18 inches at any time during the studies. In a well-water monitoring study conducted on a sand soil, chlorpyrifos and its degradates, TCP and 2-methoxy-3,5,6-trichloropyridine, were not detected (detection limits 250 ppt, 0.05 ppm, and 0.01 ppm, respectively) at any sampling interval in the water from two wells located in an orange grove in Highlands County, Florida that received three, 1 lb ai/A applications of chlorpyrifos (**40059001**).

Chlorpyrifos residues have been detected in drinking water wells in at least 12 states at levels which greatly exceed the 20 ppb lifetime Health Advisory (HA). To date, the concentration in ground water ranges up to 2090 ppb or approximately 100 times the HA. In addition, all of the detections exceed the one-day child health advisory of 30 ppb.

Data in the "Pesticides in Groundwater Database" (Hoheisel *et al*., 1992) indicate that chlorpyrifos has been detected in ground water in two other states, California and Massachusetts, in addition to the ones mentioned above. The concentrations reported in the database are very low (as would be expected from a non-termiticide use) and range from 0.05 to 0.1 ppb. These data are consistent with the ground water assessment done for the corn insecticide cluster.

The major degradate, TCP, is more mobile and persistent than the parent compound and is more likely to leach to ground water under normal use. However, it is not toxic and is not included in the chlorpyrifos tolerance.

Although moderately persistent in the environment, chlorpyrifos binds to soil. Therefore, there is a possibility that chlorpyrifos can be transported offsite on sediment borne by runoff and to be found in surface water. It has been shown (**00144906**) that chlorpyrifos will leave corn watersheds in Illinois and can be transported to ponds a short distance from the fields; quantities transported are generally less than 1% of the applied.

Modeling results highlight the relatively low potential of chlorpyrifos parent to leach to ground water from agricultural uses (concentrations of 0.1 ug/L or less in highly vulnerable ground water) but very high potential for the TCP degradate to leach (up to 85 ug/L in ground water).

Ground-water modeling results were obtained with the SCI-GROW model, which uses actual monitoring data for various pesticides at sites with sandy soils and vulnerable ground water to facilitate estimation of concentrations of other pesticides that may occur in similarly vulnerable ground water. The estimates derived with SCI-GROW are based on the high 90-day concentrations observed in shallow ground water for a set of reference compounds. These concentrations serve as both chronic and acute exposure estimates at the current time because of the difficulty in separating out seasonal differences in ground water. Concentrations would be expected to be significantly lower in the majority of the use area for chlorpyrifos where ground water is not as vulnerable to contamination. The following table summarizes chlorpyrifos residue distributions in major ground-water monitoring studies.

Chlorpyrifos Residue Distributions in Major Ground-Water Monitoring Studies							
Study Identification	Location, type of ground water	Number of samples or sites	Detection limit, ug/L	% Detections	90th percentile conc.	95th percentile conc	Highest Detection
Gilliom et al. (1998, USGS web site)	20 NAWQA study units all over U.S.: Shallow g.w., agric. areas	1130	0.004	0.26	<0.004	<0.004	0.006
Gilliom et al. (1998, USGS web site)	20 NAWQA study units all over U.S.: shallow urban wells	330	0.004	0.30	<0.004	<0.004	0.036
Gilliom et al. (1998, USGS web site)	20 NAWQA study units all over U.S.: major aquifers	1089	0.004	0.09	<0.004	<0.004	0.013
Jacoby et al. (1992, PGWDB)	CA, FL, HI, IA, IL, IN, MA, ME, MS, MN, MO, NE, NH, NY, OK, OR, PA, TX, VA	5398	variable	0.59	no data	no data	0.654

Only one study is known to be available which includes analysis for chlorpyrifos degradates in ground water. In a well-water monitoring study conducted on a sand soil, chlorpyrifos and its degradates, TCP and 2-methoxy-3,5,6-trichloropyridine (MOTCP), were not detected (detection limits 0.250 ug/L, 50.00 ug/L, and 10.00 ug/L, respectively) at any sampling interval in the water from two wells located in an orange grove in Highlands County, Florida that received three, 1 lb ai/A applications of chlorpyrifos (**MRID 40059001**). This study is not particularly enlightening, however, on the leaching potential of the degradates because of the relatively very high minimum reporting levels for these compounds. In fact, reports of any pesticide residue in ground-water at concentrations exceeding 50 ug/L (the minimum reporting limit for the degradate TCP) from agricultural applications are **extremely rare** except for a few compounds applied at higher rates. If TCP had occurred at 49 ug/L in a ground-water sample, it would not have been reported in this study. Unless it can be determined that no adverse impacts of TCP on drinking water quality can arise from concentrations well in excess of 50 ug/L, this study provides no useful information on chlorpyrifos degradates in drinking water. Assumption that vulnerable ground water used for drinking water may be contaminated with TCP at a level of up to 50 ug/L seems reasonable given that the SCI-GROW screening concentration for the citrus use is 54.5 ug/L for TCP and that citrus is commonly grown in areas with sandy soils and vulnerable ground water.

Ground Water Sources from Non-Termiticidal Uses: Acute and Chronic Exposure: Although the available monitoring data chlorpyrifos represent a large part of the United States, it is not clear that they represent the most vulnerable ground and surface waters where chlorpyrifos is used most intensely in the United States. The largest detection in about 3000 NAWQA wells across the country has been <0.04 ug/L (Table 7). The Pesticides in Ground Water Database has a maximum reported value of 0.65 ug/L. These compare with a SCI-GROW ground-water screening concentration of 0.11 ug/L for the sweet corn use. Given the large weight of support of the NAWQA data for the SCI-GROW value being sufficiently conservative, it is reasonable to conclude that the large majority of the country (> 99%) will not have ground-water usable for drinking water contaminated with chlorpyrifos parent at levels exceeding 0.1 ug/L.

For TCP, in the absence of usable monitoring data, we estimate the most vulnerable ground water usable for drinking water may be contaminated with this compound at a level of about 85.7 ug/L (the SCI-GROW value for the sweet corn use).

Ground-Water Sources from Termiticidal Uses: Results of ground-water monitoring studies confirm that contamination by chlorpyrifos is relatively rare and usually only occurs at levels in small fractions of a ug/L from agricultural uses. However, the impacts from the use of chlorpyrifos to control termites can be much greater on a local scale.

Over 60 DowElanco 6(a) 2 submissions to the Agency from 1992 to 1995 indicate chlorpyrifos has been detected in drinking water wells, cisterns, or ponds in at least 12 states, including in Alabama, Illinois, Indiana, Maryland, New York, North Carolina, Ohio, South Carolina, Tennessee, and in several unidentified locations (Table 11). All of these incidents were shown to be associated with termiticide use in the area {97% within 100 feet of the wellhead, according to an investigation by the registrant: MRID 442350-01. Thomas, J.D. and D. M. Chambers. 1997. An analysis of factors involved in suspected well contaminations by chlorpyrifos-based termiticide emulsions (Dursban TC, Equity Termiticide)}. More recently (from December 1995 to April 1998), an additional 39 incidents have been reported. In fourteen of these incidents, wells were contaminated at levels of up to 458 ug/L. No information was given on the duration of contamination at these levels.

v. Drinking Water Assessment

Concerns Over Well Contamination by Chlorpyrifos Associated With Its Termiticide Use

The number of reported incidents of substantial well contamination by chlorpyrifos associated with its termiticide use is low. Nevertheless, the level of contamination can be extremely high and it is possible (as explained below) that the number of highly contaminated wells associated with the termiticide use is substantially greater than has been reported. Such incidents are likely caused by preferential flows and possibly defects in the wells in conjunction with the high application rates and deep application associated with the termiticide use. In addition, all of the wells that have been reported to have been highly contaminated have been within 100 feet of the treated area.

The available 6(a)2 data on contaminated wells associated with the termiticide use of chlorpyrifos are provided in the following Table.

Table. Data on contaminated wells associated with the termiticide use of chlorpyrifos.

Data source	Sampled locations	# Wells	Detection limit (ug/L)	Median detect (ug/L)	Maximum detect (ug/L)	Days to reach non-detectable levels
Dow (1992, MRID 430656 & various 6(a)2 data	AL, IL, IN, KY, MD, MO, NC, NY, OH, SC, TN, VA	21	not given	81	916	7 to 160 d for 12 wells
Dow (1993-1994) 6(a)2 data	not given	9	not given	101	2090	17 d for one well
Dow (1995) 6(a)2 data	not given	3	not given	66	76	not determined
Dow (1995) 6(a)2 data	AL, IA, KY	5?	not given	56	1634	19 to 88 d for 3 wells
Dow summary report (1997) MRID 442350	25 states, 84 wells with detectable but undefined concen-trations	213	not given	not given	not given	not given

To identify wells for treatment to decrease chlorpyrifos concentrations, Dow depends on the homeowner to notify them of any well contamination associated with the termiticide use of chlorpyrifos. However, the homeowner generally does not suspect there is any contamination unless the ground water exhibits an unusual smell or appearance. In the likely event that the smell and/or visual thresholds for chlorpyrifos are substantially higher than the potentially toxic thresholds, many more wells than have been reported could have been contaminated to levels potentially hazardous to the consumers without them realizing and reporting it.

If smell and/or visual thresholds are substantially higher than toxic thresholds for chlorpyrifos, monitoring of wells for chlorprifos in the vicinity of its termiticide use should be required. In addition, the State of Illinois and Region 5 of the U.S. EPA have expressed concern over the substantial formation of chlorpyrifos oxon in wells treated for chlorpyrifos contamination. Because the oxon may also exert substantial toxicity, wells treated for chlorpyrifos contamination should also be monitored for the oxon as well as chlorpyrifos. In addition, a level of concern (LOC) for the oxon in drinking water should be developed.

In the current remediation program, Dow recommends that people can resume the use of wells treated for chlorpyrifos contamination when the chlorpyrifos concentration falls below 30 ug/L. However, HED has indicated that its level of concern (LOC) for chlorpyrifos in drinking water is much closer to 1 ug/L than to 30 ug/L. Therefore, the recommended chlorpyrifos level below which wells are considered to be safe to use again should be lowered from the current 30 ug/L. In addition, the level of the oxon may also have to be considered in determining whether it is safe to start using a treated well again.

EFED Recommended Ground and Surface Water Concentrations to HED (for Use in Their Preliminary Risk Assessment)

The dissolved concentrations of chlorpyrifos in ground and surface water that EFED recommends to HED for use in their preliminary risk assessment are listed in the following Table. Refer to the footnotes for the rationale. Recommended TCP concentrations are not provided because HED does not believe that it is toxic enough to be included in their risk assessment.

The recommended concentrations should be reasonably conservative for most drinking water for use in a preliminary risk assessment. Consequently, the estimated risks associated with them should also be reasonably conservative for most of the population. However, as discussed below, concentrations in surface water source drinking water may occasionally exceed the recommended concentrations in small watersheds with intensive chlorpyrifos use. EFED will re-evaluate its recommendations to HED for their final risk assessment.

Table: Dissolved concentrations of chlorpyrifos in ground and surface water that EFED recommends to HED for use in their preliminary risk assessment. Refer to the footnotes for the rationale.

Drinking Water Source	Exposure Duration	EFED Recommended Concentrations (ug/L)
Ground Water (for non-termiticide uses)	acute or chronic	0.007 to 0.103 [1]
Ground Water (for termiticide use)	acute	30 to 2090 [2]
Ground Water (for termiticide use)	chronic	8.3 to 578 [3]
Surface Water	acute	0.026 to 0.4 [4]
Surface Water	chronic	0.026 to 0.4 [5]

Footnote # (1): Recommended ground water concentration range for estimating upper acute or chronic risks associated with non-termiticide uses:

EFED recommends that a 0.007 ug/L to 0.103 ug/L range of SCIGROW estimated dissolved concentrations of chlorpyrifos in ground water be used by HED for estimating upper acute and chronic risks associated with non-termiticide uses. The recommended range of SCIGROW estimated dissolved concentrations of chlorpyrifos in ground water are shown in the following Table. The estimates are based upon typical and maximum total applications for various major crops as shown in the following table. The 4 crops listed in the table represent the greatest percentages of the total agricultural use of chlorpyrifos as shown in parentheses. However, a review of application rates for other agricultural uses indicate that almost all lay within the range of those for the major crops.

In all cases but citrus, the “typical” total application was provided by Dow. In all cases, the “maximum” total application were those previously used by EFED in modeling.

Based on an expanded data set and the latest EFED recommendations for developing input to SCIGROW, EFED used an average chlorpyrifos soil metabolism half-life of 28.7 days (based on 41 values) and a median K_{oc} value of 5600 (based on 27 values) in the EFED SCIGROW runs..

Table: SCIGROW estimates of dissolved concentrations in ground water associated with various major agricultural uses of chlorpyrifos.

Crop (% of total agricultural use)	Typical Total App. (lbs ai/ac)	Typical SCIGROW Concn. (ug/L)	Maximum Total App. (lbs ai/ac)	Max. SCIGR. Concn. (ug/L)

Corn (55%)	1 x 1.2 = 1.2	0.011	11 x 1 = 11 1 x 3;2 x 1.5 = 3 1 x 2 = 2 1 x 1.5 = 1.5	0.103 0.028 0.019 0.014
Cotton (6.8%)	1.7 x 0.7 = 1.2	0.011	6 x 1 = 6	0.056
Alfafa (5.9%)	1 x 0.7 = 0.7	0.007	4 x 1 = 4	0.037
Citrus (5.8%)	1 x 2.4 = 2.4	0.022	2 x 3.5 = 7	0.065

During the first phase of the NAWQA study, the USGS analyzed 3023 filtered ground water samples for chlorpyrifos. The samples were collected for a several year period during the early to mid-90s from 20 study areas throughout the U.S. The maximum reported chlorpyrifos concentration in filtered groundwater samples (reflecting approximate dissolved concentration) in the NAWQA study was 0.026 ug/L.

The maximum SCIGROW estimated dissolved concentration of chlorpyrifos in ground water of 0.103 ug/L is approximately 4 times the maximum concentration of 0.026 ug/L reported for chlorpyrifos in filtered ground water samples collected during the first phase of the NAWQA study. However, 0.026 ug/L does lay within the range of SCIGROW estimates from 0.007 ug/L to 0.103 ug/L. Furthermore, although some of the 20 study areas in the first phase of the NAWQA study overlap areas of substantial chlorpyrifos use, the NAWQA study is not a chlorpyrifos specific study designed to determine peak dissolved concentrations of chlorpyrifos in ground water. Therefore, EFED recommends that until more chlorpyrifos ground water data are collected, HED use the range of SCIGROW estimates of dissolved concentrations of chlorpyrifos in ground water in estimating upper acute and chronic risks associated with non-termiticide use.

In using the SCIGROW estimated concentrations of chlorpyrifos in ground water, HED should acknowledge that they are probably conservative for most ground waters. HED should also indicate that despite the overlap of some of the first phase NAWQA 20 study units with areas of substantial chlorpyrifos use:

(a) The maximum reported ground water concentration of chlorpyrifos in the first phase of the NAWQA study was only 0.026 ug/L.
(b) The 95th percentile was below the detection limit of 0.004 ug/L
(c) Chlorpyrifos was only detected in 0.3% of the 3023 samples analyzed.

Footnote # (2): Recommended ground water concentration range for estimating upper acute risks associated with termiticide uses:

EFED recommends that a 30 ug/L to 2090 ug/L range of dissolved chlorpyrifos concentration in ground water be used by HED for estimating a range of upper acute risks associated with termiticide use. The 30 ug/L value is the level below which Dow recommends (in their voluntary stewardship program) resuming the use of a well whose use had been suspended, and that had been treated as the result of chlorpyrifos contamination due to termiticide use. The 30 ug/L value would only be applicable in cases where the contaminated well was identified immediately after contamination, the well was removed from use, and was not used again until chlorpyrifos levels declined below the 30 ug/L level. In other highly contaminated wells, acute exposure concentrations would be higher. Although 2090 ug/L was the maximum reported value in wells contaminated by the termiticide use, it use as the upper bound of the range is justified because other reported values maximum values in the above Table containing 6(a)2 data associated with termiticide use indicate that 2090 ug/L is not an extreme outlier.

Footnote # (3): Recommended ground water concentration range for estimating upper chronic risks associated with termiticide uses:

The average annual dissolved concentrations of chlorpyrifos in wells contaminated due to termiticide use should generally be much less than the initial maximum concentrations reported due to abiotic hydrolysis and in some cases also due to substantial biodegradation. Therefore, the 30 ug/L to 2090 ug/L range of dissolved chlorpyrifos concentration in ground water recommended by EFED to HED for estimatin upper acute risks associated with termiticide use is probably too conservative for estimating the upper levels of chronic risk.

Although biodegradation may play an important role in decreasing chlorpyrifos concentrations in some wells, the low microbial activity in other wells may limit the contribution of biodegradation to the decrease in the chlorpyrifos concentration. Therefore, in attempting to arrive at more realistic but still somewhat conservative recommendations for groundwater concentrations to be used in the HED chronic assessments associated with termiticide use, EFED has chosen to use the abiotic hydrolysis rate of chlorpyrifos at pH 7 as follows:

Let C_0 be equal to a ground water concentration used in the acute assessment (e.g., 2000 ug/L, 30 ug/L). The corresponding average annual concentration recommended for use in the chronic assessment would then be given by:

$$C = \frac{C_0 \int_0^{365} \exp(-k_{hydrolysis} t)\,dt}{365} = \left(\frac{C_0}{k_{hydrolysis}(365)} \right) \{1 - \exp[-(k_{hydrolysis})(365 days)]\}$$

where

C_0 = concentration used in the acute assessment (e.g., 2090 ug/L, 30 ug/L)
C = corresponding concentration to be used in the chronic assessment = average annual concentration with an initial concentration of C_0
$k_{hydrolysis}$ = hydrolysis rate constant for chlorpyrifos at pH 7 = ln 2/72.1 days = 9.61×10^{-3} 1/day

If 2090 ug/L is used as the upper bound of the range in the upper acute assessment, the corresponding concentration recommended for use as the upper bound in the upper chronic assessment would be the annual average concentration based on an initial concentration of 2090 ug/L::

$$C = \left(\frac{2090}{(9.61 \text{ x } 10^{-3})(365)} \right) \{1 - \exp[-(9.61 \text{ x } 10^{-3})(365)]\} = 578 \text{ ug / L}$$

If 30 ug/L is used as the lower bound of the range in the upper acute assessment, the corresponding concentration recommended for use as the lower bound in the upper chronic assessment would be the annual average concentration based on an initial concentration of 30 ug/L:

$$C = \left(\frac{30}{\left(9.61 \text{ x } 10^{-3}\right)(365)} \right) \{1 - \exp[-(9.61 \text{ x } 10^{-3})(365)]\} = 8.3 \text{ ug / L}$$

Therefore, if a range of 30 ug/L to 2090 ug/L is used by HED to estimate upper acute risks associated with termiticide use, EFED recommends that a corresponding range of 8.3 ug/L to 578 ug/L be used to estimate upper chronic risks associated with termiticide use.

The above equations do not take into account additional dissipation of chlorpyrifos by ground water flow out of the well. If a conservative estimate of the ground water flow through the well (Q) can be made, the above equations can be modified to reflect it by replacing $k_{hydrolysis}$ with $k_{hydrolysis}$ + Q.

Footnote # (4): Recommended surface water concentration range for estimating upper acute risks:

A number of the 20 study areas in the first phase of the NAWQA study overlap areas of substantial chlorpyrifos use. Consequently, EFED believes that the highest reported dissolved concentration of chlorpyrifos in surface water of 0.4 ug/L in the first phase of the NAWQA study is within the upper portion of the distribution of dissolved chlorpyrifos concentrations likely to be detected in flowing water and its use is therefore appropriate for the acute assessment.

However, HED should consider using a range of dissolved concentrations in surface water (bounded by the maximum reported value of 0.4 ug/L and the 95th percentile value of 0.026 ug/L) to estimate the upper acute risks. The available data indicate that such actual concentrations probably much more closely approximate the upper range of peak dissolved chlorpyrifos concentrations in surface water source drinking water supplies than do the 11.1 ug/L to 40.6 ug/L range of PRZM/EXAMS estimated peak EECs for a 1 ha by 2 m deep pond draining a 100% cropped and 100% treated 10 ha field. However, see the caveat below.

The NAWQA study is not a chlorpyrifos specific study designed to capture maximum chlorpyrifos concentrations. Although a number of NAWQA study areas overlap areas of substantial chlorpyrifos use, others do not. In addition, many of the samples were collected at set time intervals instead of in response to runoff events (increased flow). Consequently, the maximum and 95th percentile dissolved chlorpyrifos concentrations in chlorpyrifos specific studies and in studies where most of the samples are collected in response to runoff events (increased flow) may be somewhat higher than those reflected by the NAWQA study. That should be stated if HED uses the NAWQA values in its preliminary estimates of upper acute risks.

EFED will re-evaluate its surface water concentration recommendations to HED for their final acute risk assessment to ensure against the recommendations not being conservative enough.

Footnote # (5): Recommended surface water concentration range for estimating upper chronic risks: The dissolved concentration range of chlorpyrifos in surface water that EFED recommendeds to HED for estimating upper chronic risks is also 0.26 ug/L to 0.4 ug/L which is the same as the recommendation for assessing upper acute risks. The rationale is as follows.

Maximum reported dissolved pesticide concentrations are typically less in reservoirs than in flowing water. However, annual mean dissolved concentrations in reservoirs are typically somewhat higher than in flowing waters. Therefore it would not generally be appropriate to use annual averages in flowing water as surrogates for annual averages in reservoirs. Nevertheless, annual mean concentrations in reservoirs should not be any higher (and should generally be lower) than the peak concentrations in the flowing waters that feed them. Therefore, peak concentrations in flowing water can generally serve as conservative surrogates for annual mean concentrations in the reservoirs fed by the flowing water.

Although the recommended range of 0.026 to 0.4 ug/L for estimating upper chronic risks may be overly conservative, EFED believes that it is currently justified because:

(a) The annual average dissolved concentrations in some reservoirs could be substantially higher than the annual average dissolved concentrations in flowing water.

(b) Dissolved concentrations in chlorpyrifos specific studies and/or in studies that have a large number of samples collected in response to runoff events will probably be somewhat higher than in the first phase of the NAWQA study.

Dow has indicated "The trend for highest exposure levels to occur in small lakes and reservoirs is based on data for highly mobile, relatively persistent herbicide products. This trend has not been demonstrated for an insecticide such as chlorpyrifos, which is relatively non-persistent at agricultural use rates."

There is no data cited by Dow to indicate that annual average dissolved concentrations of chlorpyrifos or similar insecticides in reservoirs are not higher than the annual average dissolved concentrations in the flowing waters that feed them. In addition, much of the dissipation observed for dissolved chlorpyrifos in fate studies appears to be due to adsorption to suspended and bottom sediment and possibly volatilization, not degradation. Therefore, chlorpyrifos could be somewhat persistent in deep reservoirs with low suspended sediment and low microbial activity.

Because of the EFED concerns described above, EFED recommends that for now, HED use the same range of dissolved chlorpyrifos concentrations in surface water for estimating upper chronic risks as is being recommended by EFED for estimating upper acute risks (0.026 ug/L to 0.4 ug/L - see footnote #4). Such values are probably overly conservative for most surface waters. However, the available monitoring data indicate they are probably much closer to upper bound average concentrations in drinking water than the 1.9 ug/L to 6.7 ug/L range of PRZM/EXAMS estimated 90-day average EECs for a 1 ha by 2 m deep pond draining a 100% cropped and 100% treated 10 ha field.

EFED will re-evaluate its surface water concentration recommendations to HED for their final chronic risk assessment to ensure against the recommendations not being conservative enough or against them being overly conservative..

3. Ecological Effects Characterization

a. Terrestrial Toxicity Assessment

EFED has adequate ecological toxicity data to assess the hazards of chlorpyrifos and its major degradation product to nontarget terrestrial organisms for dietary exposures. At present, terrestrial risk assessments are limited to dietary exposures, because quantative methods are unavailable to assess risks posed by dermal and inhalation exposures for wildlife. A considerable amount of toxicity data are available on numerous avian and laboratory mammalian species for chlorpyrifos. In addition to the standard toxicity tests, studies are available which include effects of cold stress on toxicity, small pen studies and three field studies on corn, citrus, and golf courses.

Extensive acute and subacute dietary avian test data are available on technical grade chlorpyrifos; and avian toxicity values are also available for microencapsulated and granular chlorpyrifos products and the major degradate, TCP. Avian toxicity data on these two products and the major degradate indicate that they are less toxic (i.e., less hazardous) than technical grade chlorpyrifos. Acute LD_{50} values for technical grade chlorpyrifos is available for 15 avian species with a range of LD_{50} values from 5.62 to 476 mg/kg. Two avian species have LD_{50}s less than 10 mg/kg (very highly toxic); another 8 species have toxicity values less than 50 mg/kg (highly toxic); the remaining 5 avian species have acute LD_{50} are less than 500 mg/kg (moderately toxic). The most acutely sensitive avian species are common grackle (5.62 mg/kg), ring-necked pheasant (8.41 mg/kg), common pigeons (10 mg/kg) and house sparrow (10 mg/kg). However, the house sparrow is the most acutely sensitive avian species on a milligram/bird basis (i.e., LD_{50} equal to

0.277 mg versus 0.64 mg for the common grackle). Therefore, the acute avian LD_{50} value used to assess granular and droplet risks is 0.277 mg for the house sparrow. There is no acute LD_{50} value for the American robin which is the most frequently reported avian species killed in field incidents.

Numerous subacute dietary LC_{50} values are available, but the data are limited to dietary toxicity data for only four avian species. The lowest avian subacute LC_{50} value used for assessing dietary risks is 136 ppm for mallard ducklings (moderately toxic). Avian toxicity values for formulations (i.e., emulsified concentrate (4 EC) and microencapsulated (ME 20) and the major degradate indicate less toxicity than technical grade chlorpyrifos. While some of the avian reproduction studies are inadequate to assess risks alone, together the studies are adequate to assess effects on avian reproduction. Mallard ducks were the most sensitive species and show a pattern of lethal effects on adults, reduced egg production, eggshell thinning, and reduced number of young at 60, 100, and/or 125 ppm. The risk assessment endpoint for avian reproduction is a NOEC of 25 ppm based on the mallard duck study showing 84 percent reduction in the number of eggs and 89 percent reduction in the number of young at 125 ppm, the LOAEC.

A number of mammalian toxicity values are available for mammalian laboratory species for the technical grade and some chlorpyrifos products which are adequate to assess chlorpyrifos risks to nontarget mammals. The acute LD_{50} values range from 97 to 501 mg/kg. The acute LD_{50} value used for assessing mammalian risks was 97 mg/kg with variations corrected for various body weights. The mammalian LC_{50} values range from 1,330 to 3,500 ppm and are limited to rat studies. The dietary LC_{50} value used for risk assessment is 1,330 ppm.
The mammalian reproductive endpoint used in the risk assessment is the NOEL of 10 ppm.

Several studies on contact and residue toxicity are available on honey bees and other non-target beneficial insects. The chlorpyrifos contact LD_{50} value for honey bees is 0.059 lbs ai/bee. Foliar residues from spray applications of 0.5 and 1.0 lbs ai/A may remain toxic to non-target insects for 24 hours post-treatment.

No statistically significant ($p = 0.05$) adverse effects were found on the numbers of earthworms in trefoil pastures sprayed with chlorpyrifos at 2.0 lbs ai/A.

In three chlorpyrifos field studies with corn, citrus, and golf courses sprayed or treated with granules, a number of carcasses tested positive for chlorpyrifos including birds, small mammals, two snakes, an aquatic turtle, an adult frog and an adult toad. Although the study focus was terrestrial effects, a number of fish kills were reported in two field studies (i.e., citrus and golf courses), but the sponsor has not submitted information on residue measurements for fish and water samples to the Agency.

A number of wildlife incidents associated with chlorpyrifos use have been reported which involve the deaths of mallard ducklings, geese, other waterfowl, robins and a bluebird. In most cases, the incidents occurred following home termite applications, others with lawn and golf course treatments. In some cases residue analyses of the carcasses show the presence of both diazinon and chlorpyrifos.

A number of fish kill incidents have been reported. Most reported fish kills are associated with termiticide treatments.

The most sensitive terrestrial toxicity values listed in the table below were used for risk assessment.

Summary of Terrestrial Toxicity Values Used In Risk Assessment for Chlorpyrifos			
Toxicity Category	Most Sensitive Species	Toxicity Value	Derived Toxicity Values
Mammalian Acute LD_{50}	Rat	97 mg/kg	Herbivores and Insectivores: 15 gr. 102 ppm 35 gr. 147 ppm 1000 gr. 647 ppm Granivores: 15 gr. 462 ppm 35 gr. 647 ppm 1000 gr. 3233 ppm
Mammalian Dietary LC_{50}	Rat	1330 ppm	N/A
Mammalian Reproduction NOEL	Rat	10 ppm	N/A
Avian Acute LD_{50}	House Sparrow	10 mg/kg	N/A
Avian Dietary LC_{50}	Mallard Duck	136 ppm	N/A
Avian Reproductive NOEL	Mallard Duck	25 ppm	N/A

b. Toxicity to Terrestrial Animals

I. Birds, Acute and Subacute

In order to establish the toxicity of chlorpyrifos to birds, the following tests are required using the technical grade material: one avian single-dose oral (LD_{50}) study on one species (preferably mallard or bobwhite quail); two subacute dietary studies (LC_{50}) on one species of waterfowl (preferably the mallard duck) and one species of upland game bird (preferably bobwhite quail).

Avian Acute Oral Toxicity Findings					
Surrogate Species	**% AI**	**LD_{50} (mg/kg ai)**	**MRID No. Author/Year**	**Toxicity Category**	**Fulfills Guideline Requirement***
Ring-necked Pheasant (male) *Phasianus colchicus* (female)	94.5 %	8.41 17.7	00160000 Hudson *et al*. 1984	very highly toxic	Y
Northern Bobwhite (male & female) *Colinus virginianus*	Tech.	32	41043901 Smith 1987	highly toxic	Y
Mallard Duck (female) *Anas platyrhynchos*	99 %	75.6	00160000 Hudson *et al*. 1984	moderately toxic	Y

Mallard Duck *Anas platyrhynchos*	96.3 %	476	40854701 Roberts and Phillips 1987	moderately toxic	Y

Y = Acceptable (Study satisfied guidelines/Concur; P= Partial (Study partly fulfilled Guideline but additional information is needed; S = Supplemental (Study provided useful information, but Guideline was not satisfied)

Technical grade chlorpyrifos has a range of acute oral toxicity values from very highly to moderately toxic. The guideline requirement for a technical grade, avian oral study is fulfilled.

Supplemental Avian Acute Oral Toxicity Findings					
Surrogate Species	**% AI**	**LD_{50} (mg/kg ai)**	**MRID No. Author/Year**	**Toxicity Category**	**Fulfills Guideline Requirement**
Common Grackle *Quiscalus quiscula*	94.5%	5.62	40378401 Schaefer & Brunton 1979	very highly toxic	S
Common Pigeon *Columba livia*	94.5%	10.0	40378401 Schaefer & Brunton 1979	highly toxic	S
House Sparrow *Passer domesticus*	94.5%	10.0	40378401 Schaefer & Brunton 1979	highly toxic	S
House Sparrow (male) *Passer domesticus*	94.5%	21	00160000 Hudson *et al*. 1984	highly toxic	S
House Sparrow *Passer domesticus*	99.6%	122	440571-02 Gallagher *et al*. 1996	moderately toxic	S
Red-winged Blackbird *Agelaius phoeniceus*	94.5%	13.1	40378401 Schaefer & Brunton 1979	highly toxic	S
Coturnix Quail *Coturnix japonica*	94.5%	13.3	40378401 Schaefer & Brunton 1979	highly toxic	S
Coturnix Quail (males) *Coturnix japonica*	94.5%	15.9 17.8	00160000 Hudson 1984	highly toxic	S
Sandhill Crane (male) *Grus canadensis*	99.9% 94.5%	25 - 50	00160000 Hudson *et al*. 1984	highly toxic	S
Rock Dove (male & female) *Columba livia*	94.5%	26.9	00160000 Hudson *et al*. 1984	highly toxic	S
White Leghorn Cockerel *Gallus domesticus*	99.9%	34.8	00242149 Miyazaki & Hodgson 1972	highly toxic	S
Canada Goose (male & female) *Branta canadensis*	94.5%	40 - 80	00160000 Hudson *et al*. 1984	highly toxic	S
Chuckar (female) *Alectoris chukar* (male)	99.9%	60.7 61.1	00160000 Hudson *et al*. 1984	moderately toxic	S
California Quail (female) *Callipepla californica*	94.5%	68.3	00160000 Hudson *et al*. 1984	moderately toxic	S
Starling *Sturnus vulgaris*	94.5%	75	40378401 Schaefer & Brunton 1979	moderately toxic	S

Mallard Duck (duckling) *Anas platyrhynchos* (male & female)	99 %	112	00160000 Hudson *et al*. 1984	moderately toxic	S

Supplementary acute oral studies on other birds also have a toxicity range from very highly to moderately toxic. The six most sensitive avian species, with similar LD_{50} values between 5 and 15 milligrams/kilogram, include in order of decreasing sensitivity: the common grackle, ring-necked pheasant, common pigeon and house sparrow, red-winged blackbird, and coturnix quail. Two factors are common to this grouping. First, in general, these birds have smaller body weights than the other avian species, which agrees with the scaling factors proposed by Mineau *et al*. (1996). Second, most passerine species tested are included in this grouping (i.e., grackle, sparrow, and red-winged blackbird). Based on percent of body weight consumed per day, the most susceptible avian LD_{50} for technical grade chlorpyrifos is 10 mg/kg for the house sparrow, which is used to assess risks for granular and spray-until-runoff treatments.

Formulation testing with birds may be required if there is special concern for acute toxicity. Since chlorpyrifos has been demonstrated to be very highly toxic to birds, testing was requested for two types of particulate formulations: Dursban ME20 (a microencapsulated formulation) and Lorsban 15G (a 15 % clay-based granular, agricultural formulation). The results from avian acute studies for formulated products are summarized below.

Formulation Avian Acute Oral Toxicity Findings

Surrogate Species	% AI	LD_{50} (mg/kg ai)	MRID No. Author/Year	Toxicity Category	Fulfills Guideline Requirement
Northern Bobwhite *Colinus virginianus* (male & female)	25.65 % Dursban ME 20	545	41885201 Campbell *et al*. 1990	slightly toxic	Y Microencapsulated Formulation
Northern Bobwhite *Colinus virginianus* (male & female)	15 % Lorsban 15 G	108	41043901 Smith 1987	moderately toxic	Y Granular Formulation
House Sparrow *Passer domesticus* (male & female)	15 % Lorsban 15 G	109	44057101 Gallagher *et al*. 1996	moderately toxic	S Granular Formulation

Toxicity studies are available on the two particle-based formulations. In the Dursban ME 20 study, all bobwhite deaths occurred one day after gavaging. The need for avian acute oral formulated product studies have been fulfilled for Dursban ME 20 and Lorsban 15 G.

Degradates: The major chlorpyrifos degradate, 3,5,6-trichloro-2-pyridinol (TCP), forms a large percent of the recoverable pesticide in various compartments of the environment. Therefore, a special (70-1) acute oral test with either waterfowl or upland gamebird was required to address these concerns.

Degradate Avian Acute Oral Toxicity Findings

Surrogate Species	% AI	LD_{50} (mg/kg ai)	MRID No. Author/Year	Toxicity Category	Fulfills Guideline Requirement
Northern Bobwhite *Colinus virginianus*	99.9 % 3,5,6-TC-2-P	> 2,000	41829001 Campbell, Hoxter & Jaber 1990	practically non-toxic	Y
White Leghorn Cockerel *Gallus domesticus*	?? % Na 3,5,6-TC-2-P	> 1,000	00242149 Miyazaki & Hodgson 1972	slightly toxic	S Purity Unknown

TCP is practically non-toxic acutely to birds. Results suggest that the major degradate is less acutely toxic to birds than chlorpyrifos (i.e., > 2,000 mg/kg versus 32 mg/kg). The need for an avian oral LD_{50} toxicity study on a major degradate is fulfilled for a wild bird species.

Avian Subacute Dietary Toxicity Findings					
Surrogate Species	**% AI**	**LC_{50} (ppm ai)**	**MRID No. Author/Year**	**Toxicity Category**	**Fulfills Guideline Requirement**
Mallard Duck *Anas platyrhynchos*	99 %	136	00095007 Stevenson 1965	highly toxic	Y
Mallard Duck *Anas platyrhynchos*	96.8 %	203	40854702 Roberts & Phillips 1987	highly toxic	Y
Northern Bobwhite *Colinus virginianus*	96.8 %	423	00046955 Fink *et al*. 1978	highly toxic	Y
Northern Bobwhite *Colinus virginianus*	99 %	505	00095123 Stevenson 1965	moderately toxic	Y
Northern Bobwhite *Colinus virginianus*	96.8 %	506	40854703 Roberts & Phillips 1987	moderately toxic	Y
Northern Bobwhite *Colinus virginianus*	Assumed Tech.	531	44585401 Maguire & Williams 1987	moderately toxic	Y
Ring-necked Pheasant *Phasianus colchicus*	97.0 %	553	00022923 Hill *et al*. 1975	moderately toxic	Y
Mallard Duck *Anas platyrhynchos*	96.8 %	590	00046954 Fink & Beavers 1978	moderately toxic	Y
Northern Bobwhite *Colinus virginianus*	94 %	863	44585403 Thompson-Crowley 1981	moderately toxic	Y

Supplemental Avian Subacute Dietary Toxicity Findings					
Surrogate Species	**% AI**	**LC_{50} (ppm ai)**	**MRID No. Author/Year**	**Toxicity Category**	**Fulfills Guideline Requirement**
Northern Bobwhite *Colinus virginianus*	Assumed Technical	283 - 497	44585401 Maguire & Williams 1987	highly toxic	S

Coturnix Quail *Coturnix japonica*	97 %	293	00115301 Hill and Camardese 1986	highly toxic	S
Coturnix Quail *Coturnix japonica*	97.0 %	299	00022923 Hill *et al*. 1975	highly toxic	S
Mallard Duck *Anas platyrhynchos*	97.0 %	940	00022923 Hill *et al*. 1975	moderately toxic	S
Coturnix Quail *Coturnix japonica*	41 %	492	00115301 Hill and Camardese 1986	highly toxic	S

Results from these acceptable and supplementary studies indicate that chlorpyrifos is moderately to highly toxic to avian species on a subacute dietary basis. Food consumption rates and mortality dates were checked in some six studies. In many cases, reduced food consumption was evident, especially at higher test concentrations. Most deaths occurred on Days 3 to 5 for bobwhite and Days 3 to 7 for mallards. In some cases, deaths continued to Day 8, the last day of the test. The guideline requirements for the two avian subacute toxicity tests are fulfilled.

Subacute dietary testing with formulations on avian species may be required if there is special concern for toxicity with bobwhite quail and mallard ducks.

Formulation Avian Subacute Dietary Toxicity Findings

Surrogate Species	**% AI**	**LC_{50} (ppm ai)**	**MRID No. Author/Year**	**Toxicity Category**	**Fulfills Guideline Requirement**
Coturnix Quail *Coturnix japonica*	40.7 % Lorsban 4 EC	492	00115301 Hill and Camardese 1986	highly toxic	S Emulsified Conc. Formulation
Northern Bobwhite *Colinus virginianus*	25.65% Dursban ME 20	387	41965502 Long *et al.* 1991	moderately toxic	Y Encapsulated Formulation
Mallard Duck *Anas platyrhynchos*	25.65% Dursban ME 20	803	41965501 Long *et al.* 1991	slightly toxic	Y Encapsulated Formulation

These formulation studies on birds indicate high to moderate subacute toxicity. Comparison of the LC_{50} values for these formulations with values for technical grade chlorpyrifos shows lowering of toxicity for Japanese quail (i.e., 492 ppm versus 293 and 299 ppm); a slight increase in toxicity for bobwhite (i.e., 387 ppm versus 423, 505, 531, and 863 ppm); and a slight reduction in toxicity for the mallard (i.e., 803 ppm versus 136, 203, and 590 ppm). For Dursban ME 20, all deaths occurred on Days 3 to 6 for bobwhite and Days 4 to 7 for mallards. Reduced food consumption did not occur for the microencapsulated granules at the lower test levels. The two Dursban ME 20 studies fulfill any requirement for avian subacute dietary studies for this formulation.

Degradate: EFED is increasingly concerned about the potential environmental hazard posed by major degradates. Jarvinen and Tanner (1982) identified two degradates, 3,5,6-trichloro-2-pyridinol and a chlorpyrifos oxygen analog. The major chlorpyrifos degradate, 3,5,6-trichloro-2-

pyridinol (TCP), forms a large percent of the recoverable active ingredient in various compartments of the environment. Therefore, a special (70-2) 8-day subacute oral test with either waterfowl or upland gamebird was required to address these concerns.

Degradate Avian Subacute Dietary Toxicity Findings					
Surrogate Species	**% AI**	**LC_{50} (ppm ai)**	**MRID No. Author/Year**	**Toxicity Category**	**Fulfills Guideline Requirement**
Mallard Duck *Anas platyrhynchos*	99.9 % 3,5,6-TC-2-P	> 5,620	41829002 Long, Hoxter & Jaber 1990	slightly toxic	S LC50 uncertain due to high reduction in food consumption

The mallard dietary LC_{50} study with TCP suggests low toxicity to birds. Compared to chlorpyrifos, the degradate poses a strong reduction in dietary risks to birds (i.e., > 5,620 ppm versus 136 ppm). For the purpose of risk assessment for chlorpyrifos, the need for an avian subacute dietary LC_{50} toxicity study on a major degradate is fulfilled for a wild bird species.

ii. Special Avian Tests, Acute and Subchronic Toxicity

Two published studies (acute oral and subacute dietary) were conducted on bobwhite quail to measure the effects of cold stress on toxicity. A second set of three subacute dietary studies with mallard ducks were submitted, which tested to determine the effect of decreasing chlorpyrifos residues in food on subacute LC_{50} values. A third set of dietary studies tested toxicity of Dursban granules to bobwhite and effects of food preference tests on toxicity.

14-Day old bobwhite were evaluated 4 hours after dosing with chlorpyrifos (at test concentrations ranging from 100-1000). The bobwhite held at various temperatures, showed increased mortality and increased cholinesterase inhibition at colder temperatures. Cholinesterase inhibition levels were below 43 % in all surviving birds, except those tested at 27.5 °C with doses of 50 and 66.7 mg/kg. Data are presented below. (Maguire and Williams 1987; MRID 44565402).

Temperature °C	LD50	Cholinesterase inhibition EC50
35	100 mg/kg	> 100 mg/kg
32.5	83.3 mg/kg	> 83.3 mg/kg
30	83.3 mg/kg	> 83.3 mg/kg
27.5	> 66.7 mg/kg	50 mg/kg

14-Day old bobwhite mortality was evaluated under constant and intermittent exposures to various colder temperatures while fed chlorpyrifos under subacute dietary test conditions. Under constant temperature conditions, mortality increased with decreased temperature. Intermittent exposures to colder temperatures also resulted in increasing mortality with decreasing temperature, but mortality was not as great as for corresponding constant temperatures (data below). (Maguire and Williams 1987; MRID 44585401).

Effect of Different Temperatures on Avian LC_{50}s (ppm)

Temperature °C	Constant Cold	Intermittent Cold
35	531 ppm	---
32.5	497 ppm	382 ppm
30	345 ppm	365 ppm
27.5	283 ppm	347 ppm

Three supplementary 11-day dietary studies on 14-day old mallards were conducted to assess the effects of simulated residue declines and repellency of chlorpyrifos on the toxicity to birds from exposure to treated food. LC_{50} values from two studies on the effects of daily declining residues (5-day half-life on vegetation) were 562 and 644 ppm. These LC_{50} values indicate that toxicity is reduced less than 2-fold compared to the 357 ppm LC_{50} reported for constant dietary test levels. All deaths occurred on Days 6 through 9 or 10 and food consumption levels were reduced with increasing test concentrations. When mallards were given an option of treated and untreated diets, mallards fed on both diets but demonstrated a preference for untreated foods rather than chlorpyrifos levels of 112 to 1124 ppm); no deaths occurred when birds where provide an option of an untreated diet. The amount of treated food eaten decreased with increasing concentrations of chlorpyrifos in the diet. (Fink *et al*. 1978, MRID 00046956; Fink *et al*. 1978, MRID 00095449; Fink *et al*. 1978, MRID 00046958; and Kenaga *et al*. 1978, MRID 00095446).

Two supplemental studies on granular formulations of 0.5, 1.0 and 10 % Dowco-179 were tested for toxicity and food preference with adult bobwhite quail. In the first study, a two-week dietary exposure to the 10% Dowco-179 granules produced adverse effects including: mortality, weight loss and depressed cholinesterase levels. One male and one female bobwhite (10 percent) died in the 10% granular diet group. In the food preference test, 3 males (30 percent) died in the 10% granular diet group. Adult bobwhite fed clay granules treated with 0.5 % Dowco-179 and 1.0 % Dowco-179-treated granules were reported to have little, if any significant effect, but raw data were not provided for evaluation. Results of the second study (0 and 4-weeks pre-treatments with untreated granules and 1-week exposure to 10% Dowco-179-treated and untreated granules only) indicated pretreatment weight losses for the first two weeks in all groups. During the 1-week treatment study, no mortality occurred and effects on bobwhite quail body weight and food consumption were less pronounced. Whole blood cholinesterase was depressed in treated birds 38-85 percent compared to controls. Again, raw data were unavailable for complete evaluation of the study. (Shellenberger 1971, 00095304; Shellenberger 1971; 00095305).

These studies indicate that temperature stresses increase the sensitivity of birds to chlorpyrifos by about 2 fold, including mortality and sublethal cholinesterase inhibition. Given an option of treated or untreated food, the mortality results were mixed. In one case, more birds died and in another study there was no mortality.

iii. Birds, Chronic

Avian reproduction studies may be required when birds may be exposed repeatedly or continuously through persistence, bioaccumulation, or multiple applications, or if mammalian reproduction tests indicate reproductive hazard. Chronic avian testing was required, because chlorpyrifos is persistent (180 days in aerobic soils), bioaccumulates (2730 to 3900 X), and has multiple applications with up to 22 applications on corn per growing season.

Avian Reproduction Findings						
Surrogate Species	**% A.I.**	**NOEC (ppm ai)**	**LOEC (ppm ai)**	**Statistically (P < 0.05) Significant Endpoints**	**MRID No. Author/Year**	**Fulfills Guideline Requirement**
Mallard Duck *Anas platyrhynchos* (8-week preliminary study)	96.7 %	46	100	100 ppm - 84% reduction in # of eggs	00046953 Fink & Beavers 1977	S
Mallard Duck *Anas platyrhynchos*	96.8 %	30	60	60 ppm - 46% red. # eggs red. body weight of drakes & hens	42144901 Hakin 1990	S
Mallard Duck *Anas platyrhynchos*	96.8 %	25	125	125 ppm - 40% drakes & 16% hens died; 84% red. # eggs; 9% red. eggshell thickness; 89% fewer young	00046952 Fink & Beavers 1978	Y
Northern Bobwhite *Colinus virginianus*	96.8 %	40	130	130 ppm- 27% red. # eggs	42144902 Hakin 1990	S
Northern Bobwhite *Colinus virginianus*	96.8 %	125	> 125	125 ppm - 12% reduction in # of eggs; not statistically significant	00046951 Fink & Beaver 1978	S

The avian reproductive studies on mallard ducks indicate that chlorpyrifos reduces the number of eggs laid and the adult body weights at 60 ppm. The dietary concentration was reduced from 90 ppm to 60 ppm at the beginning of week 8 due to body weight losses and mortality. Bobwhite quail reproduction results suggest that the LOEL is 130 ppm based on reduced number of eggs produced. All 5 studies indicate reductions in the number of eggs laid. Other reproductive effects found were 9 percent eggshell thinning and fewer young. Chronic effects identified include increased adult mortality and adult body weight reduction. The guideline requirement for waterfowl reproduction tests is fulfilled. Both bobwhite studies together fulfilled the guideline requirement for an upland gamebird reproduction study.

iv. Mammals, Acute and Subacute

Wild mammal testing is required on a case-by-case basis, depending on the results of the lower tier studies such as acute and subacute testing, intended use pattern, and pertinent environmental fate characteristics. In most cases, however, an acute oral LD_{50} from the Agency's Health Effects Division (HED) is used to determine toxicity to mammals (HED Tox Oneliners). The mammalian acute oral LD_{50}'s are reported in the table below.

Mammalian Acute Oral Toxicity Findings

Surrogate Species	% AI	LD_{50} (mg/kg ai)	MRID No. Author/Year	Toxicity Category	Fulfills Guideline Requirement
Rat *Rattus norvegicus*	Unknown	97- 276	41043901 Smith 1987	highly toxic	Y
Rat (female) (male) *Rattus norvegicus*	Tech.	137 163	00000179 HED oneliner 4/18/94	moderately toxic	Y
Albino Rat (male) *Rattus norvegicus*	99.0 %	151	00160000 Hudson *et al*. 1984	moderately toxic	Y
Cavy *Hydrochoerus carybara*	Tech.	501	00000179 HED oneliner	slightly toxic	Y
Rat (female) (male) *Rattus norvegicus*	?? % Dursban 44	445 prod. 530 prod.	00000187 HED Oneliner	moderately toxic	Y Formulation
Rat (female) (male) *Rattus norvegicus*	22.4 % Dursban 2E	139 211	00000186 HED Oneliner	moderately toxic	Y Formulation

The available mammalian acute oral LD_{50} values indicate that chlorpyrifos is highly to slightly toxic to small mammals on an acute oral basis. The lowest rat LD_{50} value, 97 mg/kg, in the range of LD_{50} values reported by Smith (1987), is the mammalian toxicity value used to assess acute oral toxicity and is the basis for the dietary toxicity values for herbivores, insectivores and granivores.

While a mammalian, subacute dietary test is not a guideline requirement for registration, the data are very useful to assess short-term risks to small mammals in addition to using an estimated 1-day LC50 from acute oral studies. The test method is similar to the 8-day avian subacute dietary test, except it is a 14-day study with a 5-day exposure period followed by a 9-day untreated, observation period (McCann *et al*. 1981). Mammalian LC_{50}'s are reported below.

Mammalian Subacute Dietary Toxicity Findings					
Surrogate Species	**% AI**	**LC_{50} (ppm ai)**	**MRID No. Author/Year**	**Toxicity Category**	**Fulfills Guideline Requirement**
Albino Rat *Rattus norvegicus* (male & female)	97.1 %	1330	44585409 Teeters 1981 EPA Test #114	slightly toxic	Y
Albino Rat *Rattus norvegicus* (male & female)	97.1 %	1390	44585410 Teeters 1979 EPA Test #32	slightly toxic	Y
Albino Rat *Rattus norvegicus* (male & female)	97.1 %	1780	44585411 Teeters 1981 EPA Test #119	slightly toxic	Y
Albino Rat *Rattus norvegicus* (male & female)	Unknown	2970	44585413 Teeters 1979 EPA Test #29	slightly toxic	Y

Albino Rat *Rattus norvegicus* (male & female)	97.1 %	3500	44585414 Teeters 1980 EPA Test #83	slightly toxic	Y

These mammalian subacute dietary LC_{50} values indicate that Chlorpyrifos is slightly toxic to small mammals.

v. Mammals, Subchronic and Chronic

Subchronic and chronic toxicity reported in the human health section are summarized here to assess long-term effects on nontarget mammalian wildlife. In a 90-day study, chlorpyrifos fed to rats produced a systemic NOEL of 10 ppm and LOEL of 200 ppm. The LOEL is based on reduced body weights. (MRID 40436406).

A two-generation mammalian reproduction study with rats resulted in a developmental NOEL of 1 mg/kg/day and a LOEL of 5 mg/kg/day. The LOEL is based on reduced pup body weight (10 - 11 %) and increased pup mortality (4 %). (MRID 41930301).

In two-year carcinogenic studies with chlorpyrifos in rats resulted in a NOEL of 5 ppm and a LOEL of 100 ppm. The LOEL is based upon reduced body weight in males (4 - 5.3 %) and females (3.5 - 4.9 %). (MRID 42172802).

In a 78-week oncogenicity study with mice, the systemic NOEL is 50 ppm and the LOEL is 250 ppm. The NOEL is based on decreased body weight in males (5 to 8 %). (MRID 42534201).

vi. Insects

A honey bee acute contact LD_{50} study may be required, if use(s) will result in honey bee exposure. Since chlorpyrifos is used on many crops where bees are likely to be exposed, an acute honey bee study is required.

Nontarget Insect Acute Contact Toxicity Findings

Surrogate Species	**% AI**	**LD_{50} (g a.i./bee)**	**MRID No. Author/Year**	**Toxicity Category**	**Fulfills Guideline Requirement**
Honey Bee *Apis mellifera*	Tech.	0.059	05001991 Stevenson 1978	highly toxic	Y
Honey Bee *Apis mellifera*	Tech.	0.114	00066220 Atkins *et al*. 1976	highly toxic	Y
Honey Bee *Apis mellifera*	Tech.	< 0.1 100% dead at 0.01 % solution	05011163 Harris & Svec 1969	highly toxic	S LD_{50} not determined

Sufficient information exists to characterize chlorpyrifos as highly toxic to honey bees. The guideline requirement for honey bee toxicity is fulfilled.

Two laboratory studies indicate the toxicity of chlorpyrifos residues on alfalfa foliage to different types of caged bees following application of two formulations. Residues on alfalfa foliage samples from application of Dursban 4EC at 0.5 and 1.0 lb ai/A were highly toxic through 8 hours to three bee species (honey bee, *Apis mellifera*; alkali bee, *Nomea melanderi*; and alfalfa leaf-cutter bee, *Megachile rotundata*). At 24 hours, residues on alfalfa foliage remained highly toxic to the honey bee and alfalfa leaf-cutter bee and moderately toxic to the alkali bee (Johansen *et al*. 1973, MRID 00040602). Alfalfa foliage samples with chlorpyrifos residues from an application of Dursban 2 EC on alfalfa fields at 1 lb ai/A were highly toxic to the honey bees at 3 hours when placed in cages with bees, but foliage samples were not toxic at 24 hours (Johansen and Eves 1967, MRID 00060632). These two studies fulfill the requirement for a foliar residue study.

Survival of adult lady beetles (*Stethorus punctum*) was reduced to 30 percent, 48 hours after direct application of Dursban 4EC at 0.25 lb ai per 100 gallons of water. Sufficient information is available to characterize chlorpyrifos as toxic to lady beetles, when beetles are exposed to direct application. (Colburn and Asquith 1973, MRID 00059461).

In the only field study, honey bee visitation was suppressed 46 percent for three days in alfalfa fields treated with Dursban 4EC at 0.5 lb ai/A. The overall hazard to bees was low. (Atkins and Kellum 1980, MRID 00074486).

The above four studies indicate that chlorpyrifos has short-term residual toxicity, which may remain high as long as 24 hours to honey bees and alfalfa leaf-cutter bees on alfalfa or may decline significantly between 8 and 24 hours posttreatment.

vii. Earthworms

Two supplemental published articles reported effects on earthworms in chlorpyrifos-treated trefoil pastures. Thompson (1972) reported no significant effects on earthworms in trefoil pastures after applying Dursban 2 EC at 2.0 lbs/A. Three weeks after treatment earthworms averaged 14.1 worms per quadrant and 343.5 grams fresh weight per quadrant compared to control averages of 17.9 worms and 404.6 grams, respectively. (MRID 00078524). Thompson and Sans (1974) reported results on earthworms in a southwestern Ontario trefoil pasture after a spray treatment with Lorsban EC at 2 lbs ai/A. At 3 and 52 weeks post-treatment, the mean number of earthworms and mean biomass per quadrant were 2.56 ($\pm$ 3.65) worms and 2.73 ($\pm$ 3.54) grams, respectively (controls were 2.85 ($\pm$ 3.58) worms and 2.94 ($\pm$ 3.29) grams, respectively). Chlorpyrifos residue levels in earthworms 3 and 52 weeks post-treatment were 9.66 ppm and 0.0 ppm, respectively. (MRID 00095371). While the results from these two studies were not dramatic enough to be statistically significant ($p = 0.05$), the results in **both** studies indicate reductions in the numbers of worms and reductions in fresh weight measurements compared to controls. Currently, EFED has no requirement for an earthworm toxicity test. This study would not be adequate, unless the raw data were made available for statistical analyses to validate the conclusions.

viii. Terrestrial Field Studies

While chlorpyrifos would meet the requirements for terrestrial field studies based on persistence, toxicity, and multiple applications per season, the Agency did not require the three field studies. The ability of EFED to request wildlife field studies was suspended by the OPPTS Assistant Administrator in 1992. On their own initiative, the registrant has submitted three terrestrial field studies (i.e., corn, citrus, and golf courses) in 1995 for inclusion in the Chlorpyrifos RED. A study is also available on a large pen study.

A large pen, simulated field study was conducted on turf with bobwhite quail. The turf and food (seeds) were treated with two applications of Pyrinex 4 E at 3 lbs ai/A (applied at a 2 week interval), another area was treated at 6 lbs ai/A. The maximum measured, initial chlorpyrifos levels from the 3 + 3 and 6 lbs ai/A treatments were 470, 570 and 1400 ppm on grass and 18, 21 and 30 ppm on seeds, respectively. The maximum, measured residue levels on the turf approximate the chlorpyrifos EECs (720 and 1440 ppm) but the residues on seeds are less than half of the chlorpyrifos EECs (45 and 90 ppm for seeds) predicted from the exposure nomograph used by EFED. Statistically significant effects were reported for abnormal behavior in bobwhite exposed to the 6 lbs ai/A treatment. The NOEC was reported as 3 lbs ai/A. The kind of abnormal behavior observed was not specified. Results indicated that a rash of control mortality occurred at the end of the study. Of the 6.2 % control deaths, 67% occurred during the last five days. In the low treatment, 82% of the 7.6 % deaths occurred during the same period. In contrast only 29% of the 10 % mortality in the 6-lbs ai/A occurred during that same period. The degree of mortality attributable to chlorpyrifos in the treatments is uncertain, because 9 controls also died. If mortality occurring during the last five days of the study were omitted, mortality in the high treatment might be statistically significant. According to the author, the NOEL and LOEL for this turf study are 3 and 6 lbs ai/A, respectively, based on abnormal behavior. This study would satisfy a requirement for a simulated field study on turf, if required. (Booth 1989, MRID 42144903).

In an Iowa field study on corn, chlorpyrifos was applied as either Lorsban 4E, an emulsifiable concentrate formulation, to 4 fields (4 applications per field; 1.7 to 3.4 kg/ha [1.5 - 3 lbs ai/A]) or as Lorsban 15G, a granular formulation, to 4 fields (3 applications per field; 1.1 to 2.9 kg/ha [1 - 2.6 lbs ai/A]). Chlorpyrifos levels were measured in various environmental samples. Chlorpyrifos residue levels are presented in the risk assessment section under the corn use.

Wildlife observations on treated replicates are summarized in the following table. Casualty levels found on the reference replicates include extra casualties found during the increased amount of time spent conducting additional testing on monitoring methods on reference replicates. Field investigators considered any death likely to be treatment-related if analytical analyses tested positive for chlorpyrifos residues in samples, as shown in the following table.

WILDLIFE OBSERVATIONS & DEATHS IN CHLORPYRIFOS-TREATED CORN			
Parameters	Reference Areas 1st/ 2nd/ 3rd/ 4th	Lorsban 4E Areas 1st/ 2nd/ 3rd/ 4th	Lorsban 15G Areas 1st / 2nd / 3rd

# of Censuses	45/ 28/ 39/ 30	55/ 34/ 40/ 29	53/ 40/ 31
# of bird species	60/ 49/ 50/ 43	67/ 51/ 53/ 41	61/ 48/ 41
Total birds seen	1210/ 857/1257/1088	1369/1027/1276/949	1231/ 1156/ 987
# of Species in corn	17/ 10/ 18/ 12	24/ 19/ 17/ 17	16/ 15/ 14
# Seen in corn	110/ 50/ 64/ 51	100/ 97/ 63/ 81	52/ 67/ 65
# of Dead birds	6/ 0/ 5/ 3	2/ 6/ 3/ 2	6/ 1/ 2
Analyzed/positive	0/- 0/- 1/0 1/0	0/- 0/- 0/- 1/1+1[b]	0/- 1/0[c] 0/-
# Dead mammals	3/ 6/ 1/ 0	2/ 3/ 3/ 1	0/ 4/ 3
Analyzed/positive	2/0 4/0 0/- 0/-	0/-/ 1/0/ 1/0 /1/1[d]	0/- 0/-+1[e] 2/1+1[f]
# of Dead reptiles	2/ 2/ 0/ 0	3/ 1/ 0/ 0	0/ 0/ 0
Analyzed/positive	0/- 0/- 0/- 0/-	0/-/ 0/-/ 0/-/ 0/-	0/- 0/- 0/-
# Dead Amphibia	0/ 0/ 1/ 0	0/ 0/ 0/ 1	0/ 0/ 1
Analyzed/positive	0/-/ 0/-/ 0/-/ 0/-	0/-/ 0/-/ 0/-/ 0/-	0/- 0/- 1/0[g]
Total # dead	29	27	17
Analyzed/positive	8/0	4/2 + 1[h]	4/1 +2[i]

[a] The number of post-treatment carcasses analyzed for chlorpyrifos residues and number of carcasses found to contain chlorpyrifos.

[b] Two robins were caught showing cholinesterase inhibition; one robin died with 5.8 ppm on skin, but negative for chlorpyrifos internally. The other robin survived and was released. Both are considered positive for chlorpyrifos effects.

[c] A brown thrasher was hit by a car, analysis was negative for chlorpyrifos, but it was by collected on the treat field.

[d] The carcass of a field mouse, *Peromyscus* sp. contained 0.7 ppm.

[e] An eastern cottontail rabbit was found slightly affected (cholinesterase inhibition, but it could not be caught; considered positive effect for chlorpyrifos effects.

[f] A short-tailed shrew contained 2.1 ppm in its internal tissues; a second shrew exhibited behavior typical of cholinesterase inhibition; but could not be captured; both shrews were considered positive for chlorpyrifos effects.

[g] An American toad was analyzed, but it contained no chlorpyrifos.

[h] Only four animals were actually analyzed and two test positive for chlorpyrifos, but a robin was added, because its behavior indicated cholinesterase inhibition.

[I] Only three animals were actually analyzed for chlorpyrifos; only one tested positive for chlorpyrifos, but a rabbit and a shrew were added, because their behavior indicated cholinesterase inhibition.

Carcass searches made in the corn field study found evidence of 41 pretreatment and 73 post-treatment casualties (i.e., 29 casualties on untreated fields, included 14 birds, 10 mammals, 4 snakes and an amphibian. The number of casualties reported on the untreated fields included carcasses found during supplementary activities which were not conducted on treated fields. Post-treatment casualties in Lorsban 4E, sprayed fields included 27 carcasses (i.e., 13 birds, 9 mammals, 4 snakes, and a northern leopard frog). Carcasses found in Lorsban 15G-treated fields included 17 casualties (i.e., 9 birds, 3 mammals and American toad). Only seven carcasses from treated fields (9.6%) were analyzed for chlorpyrifos. Three analyses were positive for chlorpyrifos, including a robin (5.8 ppm), a *Peromyscus* sp. (0.7 ppm), and a northern short-tailed shrew (2.1 ppm). Four of these carcasses were negative for chlorpyrifos, including a thrush, vole, shrew, and toad. Another three animals (a robin, rabbit, and shrew) were determined to be chlorpyrifos casualties based on the fact their behavior was typical of cholinesterase inhibition. Consequently, out of ten animals for which possible chlorpyrifos effects were actually determined 40% were negative and 60% were positive for chlorpyrifos residues or cholinesterase inhibition. Chlorpyrifos casualties were found in both treatments (4E and 15G). Carcass recoveries in detectability trials indicated that an average of 20.3% were recovered from field interiors, 14.9% along the perimeter, and 6.6% from adjacent habitats. Mean carcass detectability in the field interiors dramatically declined with corn growth (i.e., preplant/at-plant recovery averaged 19.3 %, emergence averaged 41.5%, whorl averaged 17.5% and tassel averaged 8.8%). Measured residues from the EC spray application on corn vegetation support exposure predictions made from the EFED nomograph for short and long grasses. The supplementary corn field study provides useful information, which generally support the residue levels and avian and mammalian mortality predicted in the above risk assessment (Frey *et al*. 1994, MRID 43483101).

In a California orange grove field study, chlorpyrifos (i.e., Lorsban 4 E) was sprayed on two plots (A and B) with 4 fields each. Each field was treated with 2 applications: 1.5 plus 6.0 lbs ai/A on plots (A) and 3.5 plus 4.0 lbs ai/A on plots (B)). Chlorpyrifos levels were measured in various environmental samples. Chlorpyrifos levels are summarized in tables in the risk assessment section under citrus uses.

Wildlife observations on treated replicates are summarized in the following table. The high casualty levels found on the reference replicates is a result of additional mortalities found during the increased amount of time spent conducting the additional activities on reference replicates. Wildlife deaths found during carcass searches were 0.5, 0.46, and 0.56 casualties per search for Treatments A, B, and reference replicates, respectively.

WILDLIFE OBSERVATIONS & DEATHS IN CHLORPYRIFOS-TREATED CITRUS			
Parameters	Reference Areas 1st / 2nd	Treatment A Areas 1st / 2nd	Treatment B Areas 1st / 2nd
# of Censuses	28 / 37	30 / 38	20 / 45
# of bird species	44 / 49	48 / 33	42 / 47
Total birds observed	708 / 1,182	893 / 1,101	543 / 1,425
Birds seen in groves	201 / 399	309 / 403	188 / 561
# of dead birds	35 / 16	27 / 16	17 / 11
Analyzed/positive	0/- / 0/-	3/0 / 2/1[a]	2/0 / 1/1[d]
# of dead mammals	10 / 8	11 / 10	10 / 4
Analyzed/positive	0/- / 0/-	4/0 / 4/0[b]	3/1[e] / 0/-
# of dead reptiles	2 / 3	1 / 2	2 / 0

Analyzed/positive	0/- / 0/-	0/- / 1/1[c]	1/0 / 0/-
# of dead Amphibia	2 / 0	1 / 3	1 / 0
Analyzed/positive	0/- / 0/-	0/- / 0/-	0/- / 0/-
Total # dead	49 / 27	40 / 31	30 / 15
Analyzed/positive	0/- / 0/-	7/0 / 7/2	6/1 / 1/1

[a] No chlorpyrifos detected in carcass of mockingbird, but 5.39 ppm was on the pelt which indicates death may have been treatment related.

[b] No chlorpyrifos detected in carcasses of ground squirrel and pocket gopher, but 1.53 ppm and 1.51 ppm was on the pelts, respectively, indicating the death may have been treatment related. It should be noted that all four analyzable mammal carcasses were found on Replicate A1 where the grove manager had put out mammal poisons prior to these collections.

[c] Chlorpyrifos residues were found in the carcass and pelt of a western rattlesnake (1.74 ppm and 6.94 ppm, respectively) indicating the death is likely treatment related.

[d] Chlorpyrifos residues were found in a young, unidentified passerine nestling (3.67 ppm in the whole body) therefore, the casualty may have been treatment related.

[e] Chlorpyrifos residues in a whole house mouse carcass was 0.610 ppm.

It was reported that, "Dead fish were found in ponds adjacent to citrus groves on several occasions during the field portion of the study. The dead fish were collected and shipped to the Sponsor. Additional samples and information collected in association with the dead fish (i.e., water and sediment samples, water temperature and dissolved oxygen) were also forwarded to the Sponsor. Since the objectives of the study did not address aquatic organisms, the fish and other aquatic vertebrates found during the study are not reported in this report. The responsibility for reporting the dead fish and other aquatic vertebrates found during this study was left with the Sponsor." Information on chemical analyses of fish and other aquatic vertebrate, sediment, and water samples have not been received from the Sponsor for review.

Out of the 192 casualties found on all citrus replicates only 21 carcasses were analyzed for the presence of chlorpyrifos. Six of the 21 carcasses (28.6 %) were found to have chlorpyrifos residues either in the carcass or on the pelt and consequently assume that they may have died from treatments. Species that tested positive for chlorpyrifos were a mockingbird, an unidentified passerine nestling, house mouse, ground squirrel, pocket gopher, and a western rattle snake. While the number of dead wildlife found during carcass searches does not show a dose-relationship with treatment levels, the number of carcasses testing positive for chlorpyrifos does (i.e., 4 carcasses at 6 lbs ai/A, 1 each at 3.5 and 4 lbs ai/A, and none at 1.5 lbs ai/A, but the number of positive carcasses are too few to verify this conclusion. These results should not be used to conclude to that 1.5 lbs ai/A does not kill wildlife. Carcasses found on reference replicates were not analyzed for the cause of death, because the authors assumed that all reference deaths represent natural deaths. According to the report, carcasses found during other activities were added to those found during carcass searches. Since most extra time was spent on reference groves evaluating other monitoring methods, the number of carcasses represent inflated numbers of death on reference plots.

Of the 119 casualties found after the first application on citrus groves, 43 % of the casualties were found in the grove interior, 31 % along grove perimeter, and 26 % in the adjacent habitats. After the second application, the number of the 73 casualties found in all replicates were from the following areas: 36 % in grove interiors, 37 % along grove perimeters, and 27 % in adjacent habitats. The results from the first and second applications are fairly consistent. The higher recovery rates reported for carcasses found in the grove interior and perimeter were easier to habitats to find dead wildlife. Carcass recoveries in detectability trials were conducted during normal carcass searches in each treatment area to determine the rate at which carcasses are removed or hidden by scavengers and the ability of searchers to detect carcasses in a search area. Carcasses were placed in grove interiors, along the grove perimeters and adjacent habitats. Carcasses recovered during other activities also were included in carcass detectability results. Carcass detectability was calculated based on the total number of marked carcasses recovered on each replicate during the study. The average percent recovery level was 23 % (138 out of 595 carcasses for post bloom tests. Carcass recoveries for each Treatment were 32.9 % for Treatment A, 19.5 % for Treatment B, and 17.4 % for reference replicates. The combined recovery rates for Treatments A and B on the three areas were 21.8 to 26.3 % for the grove interior, 24.1 to 31.3 % for the grove perimeter, and 14.0 to 18.9 % for the adjacent habitat. The citrus field study provides useful information, but it would not support a registration requirement for chlorpyrifos use on citrus, because the casualties reported from untreated orchards resulted from unequal (greater) search time on untreated orchards and control carcasses were not analyzed for chlorpyrifos residues (Gallagher *et al*., 1994, MRID 437303-01, 437067-01).

In a Central Florida golf course field study, chlorpyrifos was applied twice at 4 lbs ai/A to 4 replicates per treatment. Two chlorpyrifos formulations studied were Dursban Turf Insecticide (a liquid spray formulation) or with Dursban 2.5 Granular Insecticide. Four additional golf courses were used as controls. Two treatments were applied to each replicate golf course during the summer of 1992 at a minimum interval of 21 days between treatments. The golf courses ranged from 50 to 250 acres with treatment areas ranging from 4.7 to 7.2 acres. Chlorpyrifos levels were measured in soil and water samples. Tables with residue levels are in the risk assessment section under golf course uses with a comparison of predicted EECs.

Ninety-three avian species were observed during censuses on test replicates. Six avian species were common to all 12 test replicates and comprised 32 % of all individuals counted in censuses. The most abundant, frequently seen bird was the northern mockingbird, followed by boat-tailed grackle, blue jay, northern cardinal, and Carolina wren. Avian diversity on test replicates ranged from 0.94 to 1.30 units (Brillouin Index). The mean number of birds observed per census, on all replicates combined was 33.1. The total number of birds observed on the turf was 1499 (24.4 % of all bird observations). The species that had the highest number of individuals observed on or foraging over the turf included white ibis, boat-tailed grackle, laughing gull, cattle egret and chimney swift. Eleven mammalian species, in addition to the five species captured in small mammal traps, were seen in the study area. Eight of the eleven species were observed on the turf and one of the small mammal species was trapped on the turf. Also observed in the study area were 20 reptilian and three amphibian species. Nine reptiles and two amphibians were observed on the turf. In general, turf areas on golf courses are not attractive habitat to many wildlife species. Most wildlife observed in the study lived and fed in areas adjacent to the golf courses.

Carcasses searches were made prior to each application to remove all dead animals. Transects totaled 2400 m on each replicate with 1800 m along the turf perimeter and 600 m in the adjacent habitat. Approximately two hours were spent searching each replicate per sampling day. Evaluation of carcass removal indicates that overall, 50 % of the carcasses were removed or hidden by scavengers by the second day and 99 percent were removed by Day 4. Removal rates were similar between treatment groups. Carcass recoveries were placed on the golf courses for detectability trials. Recovery rates were 90 % on the fairway, 83 % in the rough, and 31 % in the adjacent habitat. Overall recovery rates were 77 %, 68 % and 69 % for liquid treatment, granular treatment and reference replicates, respectively. Results from carcass searches for wildlife on treated replicates are summarized in the following table.

WILDLIFE OBSERVATIONS AND DEATHS ON CHLORPYRIFOS-TREATED TURF			
Parameters	Reference Areas	Liquid-treated Areas	Granular-treated Areas
# of Censuses	60 (12/rep.)	63 (12.75/rep.)	63 (12.75 /rep.)
# of bird species	66	68	63
Total birds seen	1,755	2,059	2,336
Birds seen on turf	391	763	345
# of dead birds	3	4	2
Analyzed/positive	1 / 0	1 / 0[a]	0 / -
# of dead mammals	1	1	0
Analyzed/positive	0 / -	0 / -	- / -
# of dead reptiles	0	4	3
Analyzed/positive	- / -	3 / 1[b]	1 / 1
# of dead Amphibia	0	2	6
Analyzed/positive	- / -	2 / 0[c]	0 / -
Total # dead	4	11	11
Analyzed/positive	1 / 0	6 / 1	1 / 1

[a] Double-crested cormorant showed cholinesterase behavior, but was negative for chlorpyrifos. Assumed positive casualty due to cholinesterase behavior. Multiple acephate treatments subsequent to chlorpyrifos treatment with one acephate treatment occurring the day prior to the observation of the cormorant, confounds conclusions on the source of the cholinesterase effects in the cormorant.

[b] Florida soft-shell turtle positive casualty based on residues of 1.09 ppm.

[c] Southern toad showed cholinesterase behavior, but was < 0.5 ppm chlorpyrifos. Assumed positive casualty due to cholinesterase behavior.

"On several occasions fish were found dead in water hazards during the study, some of which were found in the study area and some which were found outside of the study area on test golf courses. The Sponsor was notified of the occurrence and provided with water, sediment and fish samples. Any fish collected were shipped to the Sponsor for evaluation along with fourteen water samples and twelve sediment samples collected from water hazards where fish were found. Since the study deals with terrestrial hazard and was not structured to evaluate aquatic hazard, the responsibility for reporting these occurrences was left with the Sponsor and are not discussed in this reported." Information on chemical analyses of the samples of fish, sediments, and water have not been received by EFED for review. The turf-treated golf course field study provides useful information, but it would not support a registration requirement for chlorpyrifos use on turf, because the casualties reported from untreated golf courses resulted from unequal (greater) search time on untreated golf courses and control carcasses were not analyzed for chlorpyrifos residues (Worley *et al*. 1994, MRID 437852-01, 437852-02).

A supplemental study evaluated the effect of chlorpyrifos sprayed at 0.25 lb ai/A to pens containing laboratory rabbits and white Peking ducks. Adverse effects were not found on mortality or body weight during the 14-day observation period. There was, however, a 50% decrease in cholinesterase activity occurred in the ducks. (Kenaga 1968, MRID 00095114).

Another supplemental published article reported the short-term effects on birds and mammals from use of chlorpyrifos (Dursban 4) applied to two ryegrass fields to control leatherjackets, a wasp-like insect, in England. Chlorpyrifos sprayed at 0.72 kg ai/ha. (0.70 lb/A) was reported to have no adverse effects on birds (12/13 species), mammals (3/1 species) or earthworms. Some rabbits appeared to feed regularly at the edge of the field after treatment. Searches and observations found no dead animals other than the leatherjackets and no abnormal behavior. Chlorpyrifos residues were measured in leatherjackets (averages 0.07-1.17 ppm). While it is possible that some species were poisoned; no carcasses were found in searches and no abnormal behavior was observed. (Clements and Bale 1988, MRID 44692001).

Summary of Terrestrial Field Studies

Results from terrestrial field studies in total indicate chlorpyrifos-related mortality for some species in every class of vertebrates, including birds, small mammals, snakes, aquatic turtle, toad, and fish). Non-target wildlife carcasses have tested positive for chlorpyrifos residues in areas treated with both granular and spray formulations. In the three major field studies, few carcasses of those found were analyzed for chlorpyrifos residues (i.e., 7 out of 44 animals in the corn study, 21 out of 116 in the citrus study, and 5 out of 22 golf course turf studies). None of the carcasses from control areas were analyzed for chlorpyrifos or other causes of death. Out of the 33 carcasses tested for chlorpyrifos, 3 out of 7 carcasses tested positive and a robin, shrew, and rabbit were reported to show behavior indicative of cholinesterase inhibition in the corn study; in the citrus study, 3 carcasses and 3 pelts tested positive out of 21 carcasses analyzed; and in the golf course turf study, 2 out of 5 carcasses tested positive and a double-crested cormorant and southern toad showed cholinesterase behavior. Fish kills were reported adjacent to chlorpyrifos-treated orange groves and golf courses.

Low carcass recovery rates reported in some chlorpyrifos fields studies and the relatively small search areas to total area treated suggest that the number of reported carcasses may grossly underestimate the number of non-target wildlife adversely affected by chlorpyrifos uses on these sites. Results from carcasses detectability tests the three field studies indicate a broad range of average recovery rates between habitat types (i.e., 5.8 to 90 percent). Open areas with little cover, like golf course, had high recovery rates, while corn fields at and after whorl stage were very low. In the golf course turf field study, carcass recovery rates were 90 % on fairways, 83% in the rough, and 31 % in adjacent habitats. In the corn field study, carcass recovery levels averaged 16.3 % for field interiors; 12.7 % along the field perimeter, and 5.8 % from adjacent habitats. In the citrus field study, carcass recovery rates averaged 24 % for the grove interior, 27.7 % for the grove perimeter, and 16.4 % for adjacent habitats. Based on the time to death in the acute oral studies, affected non-target wildlife would have ample time to move far offsite or hide in the field and adjacent habitats before dying. Except as noted above, these studies do not fulfill the requirement for field terrestrial testing with birds and/or mammals.

ix. Reports of Terrestrial Field Incidents

A number of bird kills involving mallard ducklings, geese, other waterfowl, robins and a bluebird have been reported for chlorpyrifos, most of the incidents occurred from golf course and lawn treatments. In some cases, more than one pesticide was found in the carcass. Determination of the presence of chlorpyrifos in an animal or carcass only indicates that the animal was exposed. Data are unavailable as to interpret what body burden levels of chlorpyrifos constitutes lethal or sublethal exposures. In the three field studies, researchers assumed that if chlorpyrifos residues were present, then the animals may have been affected by chlorpyrifos.

Three incidents have been reported of geese killed on golf courses treated with chlorpyrifos. An incident in New York on June 28, 1974 involved 4 Canadian geese that died while feeding and foraging on a golf course that had been treated with chlorpyrifos to control sod insects. Chlorpyrifos and diazinon were found by GC analysis in tissue and organ specimens (measurements unreported). (PIMS Report: NY 062874A).

On July 10, 1974, the New York Times reported the deaths of an unspecified number of Canadian geese and goslings which had grazed on the treated lawn and then entering the pond. The grounds of the Sperry Gyroscope Company in Lake Success, Long Island, NY, had been sprayed with Chlorpyrifos and diazinon to control chinch bugs. According to the regional supervisor of fish and wildlife for the State Department of Environmental Protection, the fowl died as a result of the spraying Dursban and diazinon in the morning.

Smith (1987) reported two incidents of geese killed on golf courses treated with chlorpyrifos alone, or in combination with diazinon. One incident involved 8 dead geese, and another 35 geese.

On October, 1989, an incident occurred in which 6 waterfowl were killed in Solano, California. Both carbofuran and chlorpyrifos were identified as present. It was not determined which pesticide was responsible for killing the waterfowl.

On January 23, 1981, approximately 75 robins were found sick or dead in and around a yard in Daytona Beach, Florida, where Dursban Plus had been applied to a lawn at 7.5 ounces per 150 gallons (0.1189 lb ai/150 gallons) to control mole crickets and/or chinch bugs. At least 16 robins were collected for AchE and chemical analysis. Brain cholinesterase activity was inhibited by 58 to 69%. The four birds analyzed by GC/MS all contained 0.48 to 3.3 ppm chlorpyrifos in their gastrointestinal tract. About the same time, 17 robins were recovered at a second residence in nearby Longwood. The robins began falling out of trees about 15 to 20 minutes after the second lawn was sprayed with 1.5 ounces of Dursban in 30 gallons of water (i.e., 0.5 percent solution). Four robins were nursed back to health, but the other 13 robins died.

On May 24, 1985, four dead robins were found in a yard in Albany, NY. The lawn had been sprayed that morning with Dursban. The dead robin and a sample of sod and grass from the treated yard were analyzed for chlorpyrifos. The robin's gizzard and its contents contained 1.05 ppm wet weight of chlorpyrifos. Sod and grass samples contained 0.62 and 7.1 ppm wet weight of chlorpyrifos. Two dogs in the adjacent yard became ill and began heaving.

Two more robin kills have been reported. One incident occurred in Tennessee in March 1991 with 32 robins killed. The other occurred in Georgia on March 5, 1991 when 14 robins were killed. Both incidents were related to termiticide use of chlorpyrifos.

On March 3, 1992, a dead bluebird was reported in Maryland. The death was related to home lawn use of chlorpyrifos.

c. Aquatic Toxicity Assessment

EFED has adequate aquatic toxicity data to assess acute and reproductive risks of chlorpyrifos to both nontarget freshwater and estuarine species of fish and aquatic invertebrates. Adequate toxicity data are also available to assess acute aquatic risks for its major degradation product. Again, the major degradate is much less toxic than chlorpyrifos. At present, aquatic risk assessments are limited to exposure to dissolved concentrations in water. Quantitative methods are unavailable to assess risks for aquatic dietary exposures (i.e., consumption of aquatic organisms by predator fish). For similar reasons, assessing risks of benthic invertebrates and fish to contaminated sediments has not been included in this document.

Extensive acute toxicity data are available on technical grade chlorpyrifos for both freshwater and estuarine aquatic organisms. Some acute studies show effects of varying environmental parameters such as different temperatures, pHs, water hardness, and salinity on toxicity. Acute toxicity data are also available for formulated products and the major degradate.

Chlorpyrifos is very highly toxic to both fish and aquatic invertebrates. Acute LC_{50} values are available on 9 freshwater fish species for technical chlorpyrifos and range from 1.8 ppb for bluegill sunfish to 595 ppb for mosquitofish. Acute LC_{50} values are available for 11 estuarine fish species and range from 0.96 to > 1,000 ppb. Fish reproduction studies with technical grade Chlorpyrifos are available on only one freshwater species, the fathead minnow (NOEC values range from 0.57 to 2.2 ppb) and three estuarine species (NOEC values range from 0.28 to 0.75 ppb). A full life-cycle test with Dursban 10 CR (i.e., 10 % ai controlled release pellets) failed to produce a NOEC at the lowest test concentration (0.12 ppb). The fathead minnow acute LC_{50} value (203 ppb) differed from the most sensitive species, bluegill sunfish, value (1.8 ppb) by more than 100 fold, hence the fathead reproductive NOEC is unlikely to be adequate to assess risks to more sensitive fish species. The fish toxicity values used in the chlorpyrifos risk assessment are as follows: 1.8 ppb for the freshwater acute LC_{50} value, 0.57 ppb for fathead minnow reproduction NOEC, and for estuarine fish an acute LC_{50} of 0.96 ppb and a reproductive NOEC of 0.28 ppb.

Acute LC_{50} values are available on 4 freshwater invertebrate species for technical chlorpyrifos and range from 0.1 ppb for *Daphnia magna* to 50 ppb for the stonefly larvae *Pteronacnarys californica*. Acute LC_{50} values are available for 6 estuarine invertebrate species and range from 0.035 for mysid shrimp to 2,000 ppb for oyster embryo-larvae. Acute estuarine LC_{50} values for two species are available for the major degradate; the degradate would not appear to be a concern, since it is considerably less toxic than chlorpyrifos. Freshwater invertebrate reproductive data is limited to one study which produced a NOEC of 0.04 ppb for *Daphnia*. The reproductive NOEC for the most sensitive estuarine invertebrate, the mysid shrimp, is less than 0.0046 ppb, which reduced the number of young produced by 85 percent.

Toxicity studies on three estuarine algal species yielded LC_{50} values ranging from 140 to 300 ppb. Direct applications of chlorpyrifos up to 240 ppb reduced the growth of several algal species which took from 9 to 17 days to recover. At direct application rates up to 1 lb ai/A in ponds 10 to 13 inches deep, an algal bloom of a blue-green algae (*Anabaena*) was observed. The authors assumed that dramatic reductions in herbivorous invertebrates caused the algal bloom.

Aquatic mesocosm and field studies with chlorpyrifos applied directly to water show dramatic effects on aquatic invertebrate populations for prolonged periods and the eradication of some invertebrate species. The results for some studies suggest adverse effects on young fish growth and possibly recruitment. A number of fish kill incidents have been reported for chlorpyrifos. Most of the fish kills appear to be related to termite treatments of buildings. A fish kill was observed in a water body adjacent to a chlorpyrifos-treated area during one of the terrestrial field studies.

I. Freshwater Fish

(a) Freshwater Fish Acute Toxicity

In order to establish the toxicity of a pesticide to freshwater fish, the minimum data required on the technical grade of the active ingredient are two freshwater fish toxicity studies. One study should use a coldwater species (preferably the rainbow trout), and the other should use a warmwater species (preferably the bluegill sunfish).

Freshwater Fish 96-Hour LC50 Toxicity Findings					
Surrogate Species	**% AI**	**LC_{50} ppb ai (95% CL)**	**MRID No. Author/Year**	**Toxicity Category**	**Fulfills Guideline Requirement**
Bluegill Sunfish *Lepomis macrochirus* (static tests)	97.0 %	1.8 2.4	40098001 Mayer & Ellersick 1986	very highly toxic	Y
Bluegill Sunfish *Lepomis macrochirus*	Tech.	3.3	00095013 Alexander 1965	very highly toxic	Y
Bluegill Sunfish *Lepomis macrochirus* (flow-thru test)	95.9 %	5.8 (4.7- 7.5)	40840904 Bowman 1988	very highly toxic	Y
Rainbow Trout *Oncorhynchus mykiss*	Tech.	3	00095013 Alexander 1965	very highly toxic	Y
Rainbow Trout *Oncorhynchus mykiss* (static test)	97.0 %	7.1 (6.0- 8.4)	40098001 Mayer & Ellersick 1986	very highly toxic	Y
Rainbow Trout *Oncorhynchus mykiss* (flow-thru test)	99.9 %	8.0 (6.8- 9.4)	00155781 Holcombe, Phipps & Tanner 1982	very highly toxic	Y
Rainbow Trout *Oncorhynchus mykiss* (flow-thru test)	95.9 %	25 (20- 32) (measured)	40840903 Bowman 1988	very highly toxic	Y
Cutthroat Trout *Salmo clarki* (static tests)	97.0 %	13.4 18.4 26.0	40098001 Mayer & Ellersick 1986	very highly toxic	Y
Channel Catfish *Ictalurus punctatus*	Tech.	13.4	00095013 Alexander 1965	very highly toxic	Y
Channel Catfish *Ictalurus punctatus* (static test)	97.0 %	280 (206 - 381)	40098001 Mayer & Ellersick 1986	highly toxic	Y
Lake Trout *Salvelinus namaycush* (static tests)	97.0 %	98 227	40098001 Mayer & Ellersick 1986	very highly toxic	Y
Lake Trout *Salvelinus namaycush* (flow-thru test)	97.0 %	244 (205 - 290)	40098001 Mayer & Ellersick 1986	highly toxic	Y
Fathead Minnow *Pimephales promelas* (flow-thru test)	99.9 %	203 (191- 217) (measured)	00155781 Holcombe, Phipps & Tanner 1982	highly toxic	Y

Supplemental Freshwater Fish 96-Hour LC50 Toxicity Findings					
Surrogate Species	**% AI**	**Parameter LC_{50} ppb ai (95% CL)**	**MRID No. Author/Date**	**Toxicity Category**	**Fulfills Guideline Requirement**
Rainbow Trout *Oncorhynchus mykiss* (static test at pH 7.1 & 44 mg/l hardness)	97.0 %	2ºC 51 7ºC 15 13ºC 7.1 18ºC < 1	40098001 Mayer & Ellersick 1986	very highly toxic toxicity increases as temperature increases	S

Cutthroat Trout *Salmo clarki* (static test at 10 ºC & 44 mg/l hardness)	97.0 %	pH 7.5 18.4 pH 9.0 5.4	40098001 Mayer & Ellersick 1986	very highly toxic toxicity increases as pH increases	S
Cutthroat Trout *Salmo clarki* (static test at 10 ºC & pH 7.4-7.5)	97.0 %	44 mg/l 18.4 162 mg/l 26.0	40098001 Mayer & Ellersick 1986	very highly toxic toxicity decreases as hardness increases	S
Lake Trout *Salvelinus namaycush* (static test at 12ºC & 44 mg/l hardness)	97.0 %	pH 6.0 140 pH 7.5 98 pH 9.0 205	40098001 Mayer & Ellersick 1986	very highly toxic inconsistent toxicity with pH levels	S
Lake Trout *Salvelinus namaycush* (static test vs. flow-thru test)	97.0 %	static 73 flow 244	40098001 Mayer & Ellersick 1986	very highly toxic toxicity greater in static vs. flow-thru	S
Lake Trout *Salvelinus namaycush* (body weight)	97.0 %	0.30 g 227 2.90 g 73	40098001 Mayer & Ellersick 1986	very highly toxic toxicity increases as fish size increases	S
Bluegill Sunfish *Lepomis macrochirus* (static tests at pH 7.4 & 272 mg/l hardness)	97.0 %	13ºC 4.2 18ºC 1.8 24ºC 2.5 29ºC 1.7	40098001 Mayer & Ellersick 1986	very highly toxic toxicity generally the same as temperature increases	S
Bluegill Sunfish *Lepomis macrochirus* (static tests at 18ºC & pH 7.1 & 7.4)	97.0 %	44 mg/l 2.4 272 mg/l 1.8	40098001 Mayer & Ellersick 1986	very highly toxic toxicity increases as hardness increases	S
Fathead Minnow *Pimephales promelas* (newly-hatched) (flow-thru test)	Tech.	140	00154732 Jarvinen & Tanner 1982	highly toxic	S
Fathead Minnow *Pimephales promelas* (newly-hatched) (static test)	Tech.	150 170	00154732 Jarvinen & Tanner 1982	highly toxic	S
Green Sunfish *Lepomis cyanellus* (36-hr static tests)	99 %	22.5 37.5 125	00095125 Ferguson, Gardner & Lindley 1966	very highly toxic fish from unpolluted area more sensitive	S
Golden Shiners *Notemigonus crysoleucas* (36-hr static tests)	99 %	35 45 125	00095125 Ferguson, Gardner & Lindley 1966	very highly toxic fish from unpolluted area more sensitive	S
Mosquito Fish *Gambusia affinis* (36-hr static tests)	99 %	215 230 595	00095125 Ferguson, Gardner & Lindley 1966	highly toxic fish from unpolluted area more sensitive	S

Acceptable and supplemental acute 96-hour toxicity tests indicate that technical chlorpyrifos is very highly toxic to both coldwater and warmwater fish species. A number of studies with technical chlorpyrifos were tested to determine the effect on toxicity of various environmental parameters, such as temperature, pH, water hardness, fish size, and static versus flow-through exposures. In general, acute toxicity of chlorpyrifos was found to increase as test temperature and pH levels increase. Results were not definitive for water hardness, fish size, and static and flow-through tests. Three fish species collected from clean waters appear to be more sensitive to chlorpyrifos than fish collected from a polluted area. The guideline requirement for acute toxicity testing of the technical grade chlorpyrifos on freshwater fish is fulfilled.

Formulation testing may be required if there is special concern for acute toxicity. Since chlorpyrifos has been demonstrated to be very highly toxic to freshwater fish, testing with typical end-use formulations which have uses which are likely to reach aquatic areas is required. While mosquito larvacidal uses are being withdrawn, aerial applications are expected to drift to aquatic areas. The minimum testing requirements are 96-hour LC50's with both coldwater and warmwater fish with the formulation.

Formulation Freshwater Fish 96-Hour LC50 Toxicity Findings

Surrogate Species	% AI	LC_{50} ppb ai (95% CL)	MRID No. Author/Date	Toxicity Category	Fulfills Guideline Requirement
Rainbow Trout *Oncorhynchus mykiss* (static test)	61.5 % Dursban 6	< 8.3 (95% dead)	00095297 McCann 1969	very highly toxic	Y Aromatic Petroleum Formulation
Bluegill Sunfish *Lepomis macrochirus* (static test)	61.5 % Dursban 6	0.8	00095321 McCann 1969	very highly toxic	Y Aromatic Petroleum Formulation
Rainbow Trout *Oncorhynchus mykiss* (static test)	25.6 % Dursban ME 20	2,200 (1,730-2,590) (measured conc.)	41885204 Mayes *et al*. 1991	moderately toxic	S unstable test concentrations
Bluegill Sunfish *Lepomis macrochirus* (static test)	25.6 % Dursban ME 20	768 (614- 922)	41885203 Mayes *et al*. 1991	highly toxic	S unstable test concentrations
Bluegill Sunfish *Lepomis macrocirus* (static test)	25 % Dursban 25W	9.5 (nominal conc.)	00095298 McCann 1970	very highly toxic	Y
Bluegill Sunfish *Lepomis macrochirus* (static test)	25 % Dursban 25W	17.3 (nominal conc.)	00095296 McCann 1970	very highly toxic	Y
Fathead Minnow *Pimephales promelas* (static test)	10 % Dursban 10 CR	122.2 (77- 167.4)	41043903 Jarvinen, Tanner & Kline 1988	highly toxic	Y
Fathead Minnow *Pimephales promelas* (newly-hatched) (flow-thru test)	10 % Dursban 10 CR	120	00154732 Jarvinen & Tanner 1982	highly toxic	S
Fathead Minnow *Pimephales promelas* (newly-hatched) (static tests)	10 % Dursban 10 CR	130 280	00154732 Jarvinen & Tanner 1982	highly toxic	S

Except for the microencapsulated formulation which was moderately toxic, all chlorpyrifos formulations indicate high to very high acute toxicity to both cold and warmwater species. Jarvinen *et al*. (1988) reported an EC50 for sublethal spinal deformities in test fish at 54.9 ppb ai (Dursban 10 CR). Results show that Dursban 6 containing petroleum distillates are very highly toxic to warmwater fish and at least highly toxic to coldwater fish. The bluegill test suggests that the inert petroleum distillates may make chlorpyrifos more toxic to warmwater fish than for the technical grade product. The guideline requirements for formulated product testing are fulfilled for Dursban 6 for both cold and warmwater fish species and for Dursban 25 W for warmwater species.

Degradate: Testing of pesticide degradates can be required for warm- and coldwater fish species when EFED is concerned for the potential environmental hazard posed by major degradates. Therefore, special (72-1) acute LC_{50} degradate tests with bluegill sunfish and rainbow trout studies were required to address these concerns. The reported water solubility level for the major degradate is 220 mg/L at pH 2-3. Water solubility values at higher pH levels are unavailable for TCP, but its solubility in water is expected to increase with increasing pH levels.

Degradate Freshwater Fish 96-Hour LC50 Toxicity Findings

Surrogate Species	% AI	LC_{50} (ppm ai)	MRID No. Author/Year	Toxicity Category	Fulfills Guideline Requirement
Rainbow Trout *Oncorhynchus mykiss*	99.7 % 3,5,6-TC-2-P	1.5	44585404 Wan 1987	moderately toxic	Y
Coho Salmon *Oncorhynchus kisutch*	99.7 % 3,5,6-TC-2-P	1.8	44585404 Wan 1987	moderately toxic	S
Chum Salmon *Oncorhynchus keta*	99.7 % 3,5,6-TC-2-P	1.8	44585404 Wan 1987	moderately toxic	S
Chinook Salmon *Oncorhynchus tshawytscha*	99.7 % 3,5,6-TC-2-P	2.1	44585404 Wan 1987	moderately toxic	S
Sockeye Salmon *Oncorhynchus nerka*	99.7 % 3,5,6-TC-2-P	2.5	44585404 Wan 1987	moderately toxic	S
Pink Samon *Oncorhynchus gorbuscha*	99.7 % 3,5,6-TC-2-P	2.7	44585404 Wan 1987	moderately toxic	S
Bluegill Sunfish *Lepomis macrochirus* (static test)	99.9 % 3,5,6-TC-2-P	12.5 (measured)	41829003 Gorzinski, Mayes, & Ormond 1991	slightly toxic	Y
Rainbow Trout *Lepomis macrochirus* (static test)	99.9 % 3,5,6-TC-2-P	12.6 (measured)	41829004 Gorzinski, Mayes, & Ormond 1991	slightly toxic	Y

The major degradate of chlorpyrifos, 3,5,6-trichloro-2-pyridinol, is moderately to slightly toxic to freshwater warmwater and coldwater fish species. These toxicity data indicate that the degradate is considerably less toxic to fish than chlorpyrifos (i.e., 1.5 ppm versus 1.8 ppb). The requirement for major degradate acute freshwater fish tests are fulfilled.

(b) Freshwater Fish Chronic Toxicity

Chronic testing with fish may be required with the technical grade pesticide, if the pesticide is persistent or if applied multiple times per season. Chlorpyrifos is relatively persistent and is registered for uses involving multiple applications and it is likely to reach aquatic habitats because of its widespread use. Therefore, the minimum required chronic fish test is a freshwater fish early life stage (ELS) or full life cycle test on the technical grade of the active ingredient (preferably with rainbow trout, bluegill sunfish, or fathead minnow).

Freshwater Fish Early Life Stage Toxicity Findings					
Species	**% AI**	**NOEC - LOEC ppb ai**	**Toxicity Effects**	**MRID No. Author/Date**	**Fulfills Guideline Requirement**
Fathead Minnow *Pimephales promelas* (32-day ELS test) (flow-thru test)	98.7 %	NOEC 1.6 LOEC 3.2 MATC 2.3	3.2 ppb 16% red. body wt.	00154732 Jarvinen & Tanner 1982	S raw data unavailable
Fathead Minnow *Pimephales promelas* (30-day ELS test) (flow-thru test)	10 % Dursban 10 CR	NOEC 1.29 LOEC 2.1 MATC 1.6	2.1 ppb 21% increase in spinal deformity	41043903 Jarvinen, Tanner, & Kline 1988	S raw data unavailable
Fathead Minnow *Pimephales promelas* (32-day ELS test) (flow-thru test)	10 % Dursban 10 CR	NOEC 2.2 LOEC 4.8 MATC 3.2	2.2 ppb 10% red. survival (not stat. sign.) 4.8 ppb 39% red. survival 32% red. body wt.	00154732 Jarvinen & Tanner 1982	S raw data unavailable

The 32-day fathead minnow early life stage (ELS) study with technical chlorpyrifos reported a NOEC/LOEC of 1.6-3.2 ppb based on statistically significant reduction of 16% in body weight. The two fathead minnow ELS studies conducted with Dursban 10 CR reported effects similar to those of the technical grade study. The NOECs for all three ELS tests are similar with a range from 1.29 to 2.2 ppb. Significant chronic effects include reductions in body weight, survival and spinal deformities. Lethargy effects were reported in two studies below the reported LOEL levels.

Freshwater Fish Full Life Cycle Toxicity Findings					
Species	**% AI**	**NOEC - LOEC ppb ai**	**Toxicity Effects**	**MRID No. Author/Date**	**Fulfills Guideline Requirement**
Fathead Minnow *Pimephales promelas* (life cycle test) (flow-thru test)	99.7 %	NOEC 0.57 LOEC 1.09 MATC 0.79	1.09 ppb 14 % red. in F_0 survival Day 12 35 % red. in F_1 survival Day 5	42834401 Mayes, Weinberg, Rick, & Martin 1993	S acetone controls sign. affected number of spawns & number of eggs
Fathead Minnow *Pimephales promelas* (life-cycle test) (flow-thru test)	10 % Dursban 10 CR	F_0 NOEC < 0.12 LOEC 0.12 F_1 NOEC < 0.12 LOEC 0.12	0.12 ppb 25% red. in F_0 survival (not sign.) 44% red. # of eggs (not sign.) 9% red. in F_0 wt. 53% red. in F_1 biomass	00154721 Jarvinen, Nordling & Henry 1982	S raw data unavailable & NOEC not found

The two fathead minnow full life cycle tests indicate that technical grade and Dursban 10 CR formulation are chronicly toxic to freshwater fish. The technical grade test reported statistically ($P < 0.05$) significant effects on adult length and adult body weight. These effects were determined to be temporal and/or were non-dose related, hence they were not used for the LOEC value. The LOEC of 1.09 ppb is based on significant reduction in survival for adults (14 % by Day 12) and offspring (35% by Day 5). In the Dursban 10 CR study, non-significant reproductive parameters, such as 25% reduction in fish maturity and 44% reduction in total number of eggs, are impacted at 0.12 ppb, the lowest level tested. The LOEC (0.12 ppb) is based on statistically significant reduced F_1 growth; the NOEC is less than 0.12 ppb. Raw data for the formulation study are not available for statistical evaluation. These studies indicate that adverse effects occur in both generations and that the second generation is more sensitive than the first generation. The guideline requirement for a chronic freshwater fish study with technical grade chlorpyrifos has been fulfilled.

The collection of chronic studies provide enough data to show what reproductive effects are likely to result from chlorpyrifos exposures. The fathead NOEC value was selected as the fish chronic endpoint rather than the MATC, because the significant effects at 1.09 ppb are reduced survival rather than growth effects. Acute fathead minnow 96-hour LC_{50}s (203 ppb for technical grade) are 110 times less sensitive than bluegill (1.8 ppb for technical grade) and other fish species. Hence, it is likely that chronic toxicity values for bluegill and many other more sensitive fish species would be less than the chronic NOEC/LOEC values reported for fathead minnows. Based on the acute-to-chronic ratio formula presented below and the fathead chronic NOEC value (0.57 ppb), the chronic NOEC for bluegill is estimated to be 0.005 ppb. Consequently, the chronic risks to freshwater fish are likely to be considerable greater than the risk quotients estimated for chlorpyrifos.

$$\text{Acute-to-Chronic Ratio:} \quad \frac{\text{acute species 1}}{\text{chronic species 1}} = \frac{\text{acute species 2}}{\text{chronic species 2}}$$

$$\text{Bluegill Chronic NOEC} = \frac{\text{acute bluegill x chronic fathead}}{\text{acute fathead}}$$

$$\text{Bluegill Chronic NOEC} = \frac{\text{1.8 ppb x 0.57 ppb}}{\text{203 ppb}} = \text{0.005 ppb}$$

ii. Freshwater Invertebrate Toxicity

(a) Freshwater Invertebrate Acute Toxicity

In order to establish the toxicity of a pesticide to freshwater invertebrates, the minimum data required of a pesticide is a freshwater aquatic invertebrate toxicity test on the technical grade of the active ingredient with early instar daphnids, amphipods, stoneflies, mayflies, or midges (preferably first instar *Daphnia magna*).

Freshwater Invertebrate 96-Hour EC50/LC50 Toxicity Findings					
Surrogate Species	**% AI**	**LC_{50} ppb ai (95% CL)**	**MRID No. Author/Year**	**Toxicity Category**	**Fulfills Guideline Requirement**

Waterflea* *Daphnia magna*	95.9%	0.10 (0.09-0.11)	40840902 Burgess 1988	very highly toxic	Y
*Daphnia magna** (static test)	97.7%	1.7 (1.0 -2.0)	00102520 McCarty 1977	very highly toxic	Y
Scud (mature) *Gammarus lacustris*	97.0%	0.11 (0.070-0.170)	40098001 Mayer & Ellersick 1986	very highly toxic	S age too old
Stonefly (2nd year) *Classenia sabulosa*	97.0%	8.2 (4.9 -14)	40098001 Mayer & Ellersick 1986	very highly toxic	S age too old
Stonefly (2nd year) *Pteronacnarcys californica*	97.0%	50 (38 -65)	40098001 Mayer & Ellersick 1968	very highly toxic	S age too old

* 48-hour EC50 (standard for daphnid tests).

Results from the acute studies indicate that technical grade chlorpyrifos is very highly toxic to several freshwater invertebrates including adult life stages. Adults are usually less sensitive to pesticides than young life stages. The guideline requirement for acute toxicity testing of the technical grade on freshwater aquatic invertebrates is fulfilled.

Formulation testing may be required if there is special concern for acute toxicity. Since chlorpyrifos has been demonstrated to be very highly toxic to aquatic invertebrates, testing with typical end-use formulations which have uses which are likely to reach aquatic area is required.

Formulation Freshwater Invertebrate 48-Hour EC50 Toxicity Findings					
Surrogate Species	**% AI**	**LC_{50} ppb ai (95% CL)**	**MRID No. Author/Year**	**Toxicity Category**	**Fulfills Guideline Requirement**
Waterflea *Daphnia magna* (static test)	25.6% Dursban ME 20	115 (28 - 435) (nom. conc.)	41885202 Mayes, Servinski, Gorzinski, & Potter 1991	highly toxic	S meas. conc. too erratic

Results for Dursban ME 20, a microencapsulated formulation, indicates that the formulation is highly toxic to aquatic invertebrates. Chemical analyses of test concentrations in the static test were too variable to assess the actual test concentrations. Since the test results are reported based on nominal concentrations, the product may be more toxic than 115 ppb. An accurate, acute aquatic invertebrate test on this formulation would permit a refined risk assessment for uses with this formulation. The value added for formulation testing is high.

Degradate: TCP forms a large percent of the recoverable active ingredient in various compartments of the environment. Therefore, a special aquatic invertebrate acute test (72-2) with the major degradate was required to address toxicity concerns.

Degradate Freshwater Invertebrate 48-Hour EC50 Toxicity Findings					
Surrogate Species	**% AI**	**EC_{50} (ppm ai)**	**MRID No. Author/Year**	**Toxicity Category**	**Fulfills Guideline Requirement**

Waterflea *Daphnia magna* (static test)	99.9 % 3,5,6-TC-2-P	10.4 (measured)	41829003 Gorzinski, Mayes, & Ormond 1991	slightly toxic	Y

The major degradate of chlorpyrifos, TCP, is slightly toxic to freshwater invertebrates. This data suggest that the major degradate is considerably less toxic to freshwater invertebrates than chlorpyrifos (i.e, 10.4 ppm versus 0.1 ppb). The guideline requirement for a major degradate test for an acute freshwater invertebrate is fulfilled.

(b) Freshwater Aquatic Invertebrate, Chronic Toxicity

Chronic aquatic invertebrate toxicity testing is required, if the pesticide is persistent or if it is applied multiple times per season. Chlorpyrifos is relatively persistent and is registered for uses involving multiple applications per season and it is likely to reach aquatic habitats because of its widespread use. Therefore, The minimum testing required to assess the chronic toxicity of a pesticide is a freshwater aquatic invertebrate toxicity test on the technical grade of the active ingredient (preferably a 21-day life cycle test with first instar *Daphnia magna*).

Freshwater Aquatic Invertebrate Life Cycle Toxicity Findings

Surrogate Species	% AI	NOEC - LOEC ppb ai	Toxic Effects	MRID No. Author/Year	Fulfills Guideline Requirement
Waterflea *Daphnia magna* (static test) (nominal conc.)	97.1%	NOEC 0.04 LOEC 0.08	0.08 ppb 100% reduction in F_0 survival 100% reduction in number of offspring	41073401 McCann 1979 Test # 2405	Y

Results from the daphnid chronic study indicates that chlorpyrifos is chronically toxic to freshwater aquatic invertebrates. Test concentrations were not measured. The guideline requirement a chronic toxic test with the technical grade chlorpyrifos for freshwater aquatic invertebrates has been fulfilled.

iii. Amphibian, Acute Toxicity

Toxicity tests on amphibians are not required. It is assumed that acute oral toxicity data for birds and acute toxicity data for fish will protect adult and aquatic life stages of amphibians, respectively.

Supplemental Amphibian Oral LD_{50} Toxicity Findings

Surrogate Species	% AI	LD_{50} mg/kg (95% CL)	MRID No. Author/Date	Toxicity Category	Fulfills Guideline Requirement
Bull Frog *Rana* sp. (male adults)	94.5 %	> 400	00160000 Hudson, Tucker & Haegele 1984	demonstrates toxicity	S too few animals

Chlorpyrifos on an oral basis is at the most moderately toxic to amphibians. These data suggest that avian acute toxicity is protective of adult amphibians.

Amphibian LC_{50} Toxicity Findings					
Surrogate Species	**% AI**	**LC_{50} ppb ai (95% CL)**	**MRID No. Author/Date**	**Toxicity Category**	**Fulfills Guideline Requirement**
Toad *Bufo americanus* (small tadpole) (24 hr LC_{50})	?? %	1	???????? Whitney 1965 (Dow Chem. Co.)	demonstrates toxicity	S
Toad *Bufo vulgaris formosus* (larvae) (24-hr LC_{50}s)	?? %	pH 5.0 13,000 pH 6.0 15,000 pH 7.0 16,000 pH 8.0 15,000 pH 9.0 16,000 pH 10 15,000	44692201 Mayer, Jr. *et al*. 1992	demonstrates toxicity	S
Leopard Frog *Rana pipiens* (tadpole) (with hind legs) (24 hr LC_{50}	?? %	3,000	???????? Whitney 1965 (Dow Chem. Co.)	demonstrates toxicity	S
Leopard Frog *Rana pipiens* (adult) (24 hr LC_{50})	?? %	30,000	???????? Whitney 1965 (Dow Chem. Co.)	demonstrates toxicity	S

Rather than ignore these toxicity data which in one case is more toxic than any fish acute value, it is assumed that the purity of the test material in these amphibian LC_{50} studies are technical grade (i.e., about 90 % or more). If the tested formulation contained less active ingredient than a technical grade, the results would be more toxic than reported and the risks greater than estimated. Results from these acute aquatic test indicate that chlorpyrifos is very highly toxic to larval amphibians. Small toad tadpoles appear to be more sensitive to chlorpyrifos than older life stages. Water pH has little effect on the toxicity of chlorpyrifos to toad tadpoles. The fact that young tadpoles are equal to or more sensitive to chlorpyrifos as the most sensitive fish species raises concerns for assessing risks in shallow waters which are a typical habitat for frogs and toad tadpoles. The toad tadpole 24-hour LC_{50} value (1 ppb) is slightly more toxic than the most sensitive fish species (bluegill LC_{50} 1.8 ppb).

iv. Freshwater Microcosm Toxicity

Dursban 2E (22.4% ai) was applied once at 0.19, 0.5, 5.0 and 20 ug/l (ppb) to mixed-flask culture microcosms which match the test concentrations in pond studies. Results during the nine-week studies from the two microcosm tests were comparable both in magnitude and the species affected. Significant ($P \leq 0.05$) effects occurred at all test concentrations (LOEC 0.19 ppb). At 0.19 ppb, zooplankton and macroinvertebrate populations were strongly affected. At 0.5 ppb, amphipods and cladocerans were virtually eliminated from the microcosms for most of the season. Copepod populations were affected at 5 and 20 ppb and ostracod populations were affected at 20 ppb were less sensitive. Single-celled algae increased during the first two weeks, probably as a result of reduced grazing by planktonic herbivores, like cladocerans whose populations were reduced. Recovery for the various species occurred at different rates; amphipods did not recover. This microcosm study provides useful information on the toxic effects of chlorpyrifos. (Shannon, Yount, and Flum 1989; ORD; MRID 44692101).

A set of chlorpyrifos microcosm tests were submitted to assess effects from simulated applications for spray drift, runoff, and combinations of spray drift and runoff. Chlorpyrifos (Lorsban 4E (41.2% ai) was applied at five treatment levels (3 replicates each) as a spray on the surface of tanks to simulate spray drift or poured in as a clay slurry to simulate runoff. Sprayed treatments were applied once at levels of 0.03, 0.1, 0.3, 1.0 and 3.0 ug/l simulating 0.05 to 16 percent spray drift from 1 lb/A application. One replicate of the microcosm was treated with 10 ug/l. Three clay slurry treatments at 0.03, 0.1, 0.3, 1.0 and 3.0 ug/l simulated runoff loadings from 0.005 to 0.5 percent of a 1 lb/A at 14-day intervals; the loading levels assume a 10:1 watershed to pond area ratio. A third set of tanks simulated three combinations of spray and slurry treatments. The first combination was sprayed three times at 1.0 ug/l (simulating 0.5% drift) at two-week intervals and three alternating simulated runoff slurry treatments applied at 0.6 ug/l (simulating 0.1% runoff) 7 days after each spray treatment. The second and third combinations were sprayed six times at weekly intervals at 0.3 ug/l (1.63% drift) and 1.0 ug/l (0.5% drift) alternating with six simulated runoff applications at 0.6 ug/l applied 4 days after spraying. (Giddings 1993, MRID 43216401 and Giddings 1993, 43216402).

Results from a single spray treatment simulating 0.05 and 0.16% drift caused few significant ecological effects. A 0.5% simulated drift treatment caused temporary reductions in many groups of invertebrates, but fish were unaffected. A simulated treatment at 1% drift caused longer-lasting effects on invertebrates and reduced fish growth and biomass. Simulation of 5% drift caused persistent effects on nearly all invertebrate taxa and significantly reduced the survival of fish. A 16% simulated drift treatment killed all bluegills. (Giddings 1993; MRID 43216401).

Three slurry treatments at 0.05% runoff caused persistent reductions in the populations of many invertebrates. Three 0.16% simulated runoffs reduced fish growth and biomass, as well as invertebrate abundance. Three 0.5% simulated runoffs caused nearly complete fish mortality. (Giddings 1993, MRID 43216401).

Combinations of simulated spray drift and runoff produced mean half-lives of 7 days with a range of 1.35 to 8.5 days. Chlorpyrifos levels in sediments were about 3 to 10X higher than in water, and did not decline consistently over time. Zooplankton were at least temporarily affected in all treatment groups; cladocerans were the most sensitive zooplankton taxa and some copepods (*Diaptomus*) and rotifers (*Keratella*) were also sensitive. Benthic macroinvertebrates were affected in all treatment groups. Bluegill survival and total biomass were statistically significantly affected only in the highest treatment (6 simulated applications each of 0.5% drift and 0.1% runoff). (Giddings 1993, MRID 43216402).

These aquatic microcosm studies provide useful information on the biological effects of chlorpyrifos from applications simulating direct application, spray drift, runoff, and various combinations of spray drift and runoff. There is no guideline requirement for microcosm field studies under FIFRA.

v. Simulated Freshwater Field Toxicity

A number of simulated aquatic field tests have been conducted on artificial ponds, limnocorrals and artificial streams. Results of these studies indicate adverse effect on mallard ducks, some fish species, and many aquatic invertebrate species.

Four applications of chlorpyrifos at 2-week intervals to replicate artificial ponds (10-13 inches deep) were made at rates of 0.01, 0.05, 0.1 and 1 lb ai/A to determine effects on mallard ducks, mosquitofish and nontarget aquatic insect populations. Artificial ponds were hand-sprayed at 0.01, 0.05, 0.1 or 1 lb ai/A (four times each at 2-week intervals). The mallard ducks (6 to 7 weeks old) were held in pens surrounding the ponds. Mallard deaths were 33 to 50 percent in treatment ponds versus no deaths in controls. The absence of a dose-response relationship for mallard mortality is confounding (see summary of duckling mortalities below). This study shows that treatment of pond water and adjacent vegetation at levels as low as 0.01 lb ai/A may cause significant mortality to young, stressed mallards. (Hurlbert *et al*. 1970, MRID 00024400).

		Treatment lbs ai/A			
	controls	0.01	0.05	0.1	1.0
% Duck Mortality	0	50	33	43	44

Cladacerans were the most sensitive species with reductions at all treatment levels. A copepod was also affected at all treatments. Caged mosquitofish deaths exceeded control deaths and generally increased with increasing treatment. By Day 7, fish deaths were 10, 17, 12, 20, and 100 percent in the control, 0.01, 0.05, 0.10, and 1.0 lb ai/A, respectively. The number of uncaged fish increased after treatment in all treatments except at 1 lb ai/A. This study indicates adverse effects on birds, fish, and nontarget aquatic invertebrates at rates as low as 0.01 lb ai/A, the lowest treatment level. (Hurlbert *et al*. 1970, MRID 00024400).

Macek *et al*. (1972) found that when Dursban was applied directly to experimental ponds, mortality occurred to bluegills and largemouth bass. (MRID 00095366).

Use Rate	Water conc. (ppb) after trt.		Percent Mortality	
lbs ai/A	Day 1	Day 35[1]	Bluegill	Largemouth Bass
0.01	0.97-1.02	0.56-0.63	3	10
0.05	2.37-2.39	1.29-2.03	55	46

[1] Day 1 after first treatment and Day 13 after second treatment

Eaton *et al*. (1984, MRID 00154717) tested the effects of continuous exposure and pulsed dosing on fathead minnows and bluegills in artificial streams (520 meters long) from May 19 through August 27, 1981 (100 days). Three streams were used, 1 continuous, 1 pulsed and 1 control. In the continuous exposure, measured concentrations ranged from 0.12 ppb during the first 2 weeks (5/19-6/9) to 0.47 ppb during the last 4 weeks (7/24-8/27). No effects were observed to either bluegills or fathead minnows. In the pulsed-dosed stream, concentrations ranged from about 1 ppb after the first two pulses (5/9 & 6/2), about 2 ppb after the third pulse (6/16) and from 4 to 7 ppb during doses 4-8 (6/3 - 8/25). Toward the end of the study (8/18 & 8/26) fathead minnows began exhibiting slight to moderate bending of, or shortening of, the caudal region. Species diversity was decreased by similar amounts in both streams. Amphipods were severely affected in both continuous and pulse-dosed streams. (MRID 00154717).

A limnocorral study was conducted to develop aquatic testing methods by EPA Duluth Environment Research Laboratory using chlorpyrifos (Siefert *et al*. 1988). For 1 year, the populations of phytoplankton, zooplankton, juvenile bluegill sunfish, larval fathead minnows, juvenile green sunfish, macroinvertebrate and macrophyte communities were monitored to evaluate the effects of direct spray treatments of chlorpyrifos to a natural aquatic system. Twelve littoral enclosures measuring 5 m X 10 m were built in a 2 hectare pond. The average maximum depth of enclosure was 1.1 meter. The enclosures included natural shoreline, littoral zone and sediments. Two replicate enclosures each were tested for controls and the low treatment; four replicates each were tested for medium and high treatments. Chlorpyrifos was sprayed evenly over the enclosure water surface on June 16, 1986 to achieve the following peak concentrations 0.5, 5.0 and 20 ppb. Actual measured peak concentrations one hour after treatment, were 0.51 (low), 6.29 (medium), and 32.0 (high). All enclosures were treated identically except for the chlorpyrifos treatment rate and the addition of green sunfish to one-half of the enclosures (i.e., they were added to one control enclosure, one low-concentration enclosure and to two each of the medium- and high-concentration enclosures).

No significant effects were found in the following monitoring areas: water chemistry (e.g., pH, dissolved oxygen, etc.); leaf liter decomposition and nutrient cycling; and macrophyte biomass. Chlorpyrifos analytical studies indicate that maximum concentrations in water 1 hour after direct application to water, followed by a rapid decrease in concentration. Concentrations in sediments reached maximum 1 day after application in the high treatment, and 4 days after application in the medium and low treatments. By Day 64 the sediments contained more chlorpyrifos than the water. Most sediment chlorpyrifos (75 to 90 %) remained in the top centimeter, and it was detectable 420 days after application.

Statistically significant (P = 0.05) reductions at the lowest treatment level were found in abundance of some species of microinvertebrates, insects, amphipods and bluegills within 4 days, and larval fathead minnow and green sunfish growth by Day 15 or 16. Information from both *in-situ* bioassays and sampling of endemic communities and populations indicate that chlorpyrifos applied at these test concentrations could severely reduce or eliminate many natural populations of macroinvertebrates. Abundance of both invertebrates (i.e., cladocerans, copepods, rotifers, insects and amphipods) and larval fathead minnow growth were statistically (P = 0.05) reduced at the low treatment level (0.51 ppb). Invertebrate NOEC and LOEC are < 0.51 ppb and 0.51 ppb, respectively.

The relative sensitivities of bluegill sunfish and fathead minnows to chlorpyrifos tested in the laboratory were confirmed with the enclosure tests - an example of the field validation. Indirect effects of the pesticide application became apparent with the change in the diets of endemic fathead minnow larvae in the treated enclosures. While chlorpyrifos killed 1.7 percent of the bluegill sunfish in low treatment enclosures (0.51 ppb, peak concentration), the deaths were not statistically significant (P = 0.05) from controls. The LOEC for direct acute toxicity to fish (bluegill sunfish) is the medium treatment level, with a peak concentration of 6.29 ppb. The statistical NOEC and LOEC for bluegill and green sunfish survival are 0.51 and 6.29 ppb (1 hour peak measurements), respectively.

While the statistically significant growth reduction in fathead minnows in the low treatment was reportedly transient, the growth rate for wet weight which differed by more than 50% through the remainder of the test appears biologically, if not statistically, significant . Only two replications in the controls and low treatment limit the sensitivity of statistical tests to identify significant differences. The LOEC and NOEC for fathead minnow growth study are 0.51 ppb and $\leq$ 0.51 ppb, respectively.

The authors concluded that the field invertebrate populations were reduced more severely than would be predicted by acute LC_{50} laboratory values. The basis for their conclusion was a comparison of the statistically significant (P = 0.05) reductions in abundance of 19 of the 55 invertebrate taxa in the low treatment enclosure to abundance reductions suggested by LC50 values from the literature, only 10 out of the 55 taxa should have been reduced. EFED concludes that the LOEC for this study is 0.51 ppb based on statistically significant reductions in abundance of 19 out of 55 invertebrate taxa and statistically and biologically significant reductions in growth in larval fathead minnows. An NOEC could not be determined in this study for invertebrates or fish. (MRID 41205403).

The requirement for simulated microcosm studies are no longer be required, except in unusual circumstances (Fischer 1992).

vi. Freshwater Field Toxicity

The requirement for field studies has been suspended, except in unusual circumstances (Fischer 1992). The very high acute, chronic toxicity of chlorpyrifos and former registrations for mosquito larvacidal use have lead to many aquatic field studies. In addition to the above microcosm and simulated field studies, a number of field studies have been conducted with natural ponds, lakes, and rice fields to determine primary and secondary (ecological) effects and effects from aquatic insect control uses. The results of these studies indicate adverse effect on some fish species and many aquatic invertebrate species. Other reports have not been reviewed as the field studies, because they varied so greatly from recommended test procedures.

(a) Fish Studies

Two chlorpyrifos formulations were applied at 0.05 lb ai/A to a natural 1.8 acre pond (2 feet deep) in Minnesota to determine effects on nontarget species from mosquito larvicide treatments (Siefert 1984, MRID 00154727). A slow-release 1% formulation, Clarke Granular Larvicide, was applied on June 1 and June 20, 1983; Dursban 2E (22.4% a.i.) was applied on July 12, 1983. The responses of 200 caged bluegill, white suckers and fathead minnow were monitored. A 1-acre reference pond was established as a control. Three treatments were made. The white suckers in both treatment and reference ponds died by the end of June, presumably because of unsatisfactory habitat or disease problems. Bluegill survival was essentially unaffected by the first two treatments, but was significantly reduced (50 to 70 percent) compared to 0% control mortality after the third treatment. There was 100% mortality of unacclimated bluegill (new fish added to the cages where the white suckers had all died) exposed to only the final (EC) treatment (control fish placed in these cages prior to final treatment experienced 27% mortality). This study shows that 0.05 lb ai/A when applied as an EC is likely to kill sensitive fish (such as bluegill). Because of the high control mortality, the fathead minnow results were not useful. Residues in water following the granular treatments did not exceed 0.31 ppb. Residues in the water column following the EC treatment were 4.7, 3, 1.2, and < 0.05 ppb at 0, 2, and 4 hours and throughout the remainder of summer, respectively.

Miller (1966, MRID 00095128) found that direct application to natural ponds caused mortality to fish. At 0.025 lb ai/A caused no mortality to caged bluegill (5-6 inches long) but did result in mortality to small uncaged bluegill (1-2 inches) in shallow water. At 0.25 lb ai/A, all caged bluegill died and a large number of uncaged aquatic organisms were dead or dying 24 hours after treatment.

Other reports are available presenting information on the effects of chlorpyrifos on fish under field conditions. Davey et al. (1976, MRID 00092775) reported application of 0.10 lb ai/A of an EC formulation to 0.01 acre rice plots caused 74.4 % mortality to green sunfish and < 10% mortality to mosquitofish. These percentages were corrected for control mortality.

Linn (1968, MRID 44585405) reported 100 % mortality of caged green sunfish within 24 hours after direct, low volume application of 0.05 lb ai/A to a shallow pond. Wild bluegill and fingerling carp also died during this period. In a second test in a rice field, 20 % of the caged green sunfish died after 48 hours after direct application of 0.025 lb ai/A and 100 % fish died in the field sprayed with 0.05 lb ai/A. Control mortality was reported as 10 %.

Bischoff *et al.* (1972, MRID 44585406) reported mortality levels to caged bluegills in California rice fields sprayed at 0.0167 lb ai/A to control mosquito larvae in 1970. In the five cages, bluegill mortalities of 0, 0, 0, 33, and 60 % occurred within 72 hours.

Washino *et al*. (1972, MRID 00095370) investigated the effects of low volume Dursban sprays on caged bluegill and mosquitofish. Applications were sprayed directly to water in rice fields at 0.0125 and 0.0167 lb ai/A for mosquito control. Bluegill mortality was 32% after 3-5 days while mosquitofish mortality was only 0.5% (compared to 0 control mortality).

Summary of Fish Mortality from Field Studies									
Author/Date MRID #	Application Rates in lbs ai/A								
	0.01	0.015	0.02	0.025	0.05	0.1	0.2	0.25	1.0
Macek *et al*. 1972 00095366	3% [B] 10% [L]				46% [B] 55% [L]				
Miller 1966 000095128				MORT [B]				100% [B] MORT [?]	
Siefert 1984 00154727					50- 70% [B]				
Davey *et al*. 1976 00092775						74% [G]			
Linn 1968 44585407				20% [G]	100% [G]				
Hurlbert *et al*. 1970 00024400	17% [M]				12% [M]	20% [M]			100% [M]
Washino *et al*. 1972 00095370		0.5% [M] 32% [B]							
Estuarine Studies:									
Ludwig *et al*. 1967 00095130				0% [M]	47% [3M] 0% [C]				
Miller 1966 00104696					100% [S] 17% [C] 32% [P]				
Thirugnanam & Forgash 1977 44585408				19% [F]					
Wall & Marganian 1971 05000928					0% [K]	0% [K] 0% [S]	MORT [K]		

L = largemouth Bass M = Mosquitofish % = percent mortality of caged fish 0 = No mortality observed
B = Bluegill K = Killifish ? = Species Not Identified 3M = 3 species of minnows
G = Green Sunfish F = Mummichogs MORT = mortality of uncaged fish C = Mullet
S = Flounder P = Molly

These field studies, including those studying estuarine species, suggest that occasionally applications as low as 0.01 lb ai/A will cause mortality to fish. However, if applications reach 0.05 lb ai/A, fish mortality is expected to be extensive. It should be noted that most of these reports did not provide measured concentrations or water depths.

These studies would not fulfill the requirement for field testing effects to fish for terrestrial use sites such as agricultural crops or livestock treatment since the route of exposure (i.e. direct application) is not the same as that which would occur through runoff. The results do suggest that hazard will occur at the expected levels of exposure from these other uses.

(b) Invertebrate Studies

Field studies were required to determine exposure or effects to aquatic invertebrates (section 72-7). Based on the toxicity of chlorpyrifos, both acute and chronic effects were expected under typical use conditions.

Ali and Mulla (1978, MRID 05000841) treated two lakes with granular chlorpyrifos at 0.19 lb. ai/A. Zooplankton and benthic invertebrates were sampled to determine changes in populations following exposure to chlorpyrifos. Cladocerans such as *Daphnia pulex*, and *D. galeata* were reduced substantially during the first week but recovered after 3 weeks. The ostracod (*Cyprinotus* sp.) populations were reduced 60 to 90 percent the 4th week after treatment and the effects remained for about 6 weeks. The amphipod (*Hyalella azteca*) was completely eliminated during the 2nd or 3rd week posttreatment and recovered at a slow rate in subsequent weeks. The cladoceran *Bosmina longistris* also was "considerably" reduced. The copepods *Cyclops* sp., *Diaptomus* sp. and the benthic naidid worms were not observably affected.

A 40% EC formulation of chlorpyrifos was applied at 0.025 and 0.25 lb ai/A to four replicate ponds (24 cm deep) per dose in central California to determine effects on phytoplankton, zooplankton, and insect populations (Hurlbert *et al*. 1972, MRID 00095365). Tabular results indicated stimulation of an algal bloom of blue-green alga (*Anabaena*) in some high-dose ponds and a reduction in populations of predaceous insects. Other algae and diatom blooms also occurred. Six weeks after treatment, phytoplankton was 2X and 16X control levels in the low and high-dose ponds, respectively. There appeared to be an overall disruption of algae and aquatic invertebrate population dynamics for up to 6 weeks after chlorpyrifos treatment.

Hurlbert *et al*. (1970, MRID 00024400) and Hurlbert *et al*. (1972, MRID 00095365) reported the effects of chlorpyrifos on invertebrates in artificial ponds. Chlorpyrifos was applied 4 times at 2-week intervals directly to artificial ponds at rates ranging from 0.01, 0.05, 0.1 and 1 lb ai/A. Two ponds with a surface area of 27 X 55 feet (10-13 inches deep) were treated at each level. There were two control ponds for a total of 10 ponds in all. Invertebrates were collected with nets. Invertebrates observed included *Asplanchna brightwelli* (large rotifer), *Moina micrura* (cladoceran), *Cyclops vernalis* and *Diaptomus pallidus* (copepod), and an insect *Corisella* spp. *M. micrura* was the most sensitive, experiencing reductions at all treatment levels. *C. vernalis* was also reduced at all treatment levels. *Corisella* populations remained fairly high in the control ponds throughout the study. Increased treatment reduced numbers, with some recovery at lower levels (0.01 and 0.05 lb ai/A) after the first few treatments. Recovery of reduced populations was minimal at the higher levels after the first treatment and at the lower levels after the third and fourth treatments.

Macek *et al*. (1972, MRID 00095366) studied chlorpyrifos effects on aquatic invertebrates in experimental ponds sprayed at 0.01 and 0.05 lb ai/A. The high treatment reduced total number of insects colonizing plate samplers by three-fourths, eliminated caddisflies and severely reduced mayfly populations. Residues in pond water following two applications each of 0.01 and 0.05 lb ai/A were reported. Second application was 34 days after first.

Residues (ppb) (mean of five samples)in 4 ponds

Rate	Days after First Treatment							
lb/A	1	3	7	28	35	37	41	47
0.01	1.02	0.24	0.23	0.24	0.56	0.35	0.06	0.04
0.01	0.97	0.37	0.17	0.09	0.63	0.41	0.08	ND
0.05	2.39	1.68	0.92	0.20	2.03	1.09	0.47	0.05
0.05	2.37	1.77	1.23	0.10	1.29	0.92	0.40	0.07

Roberts (1973, MRID 00095368), Nelson and Evans, Jr. (1973, MRID 00095338), and Roberts and Miller (1970, MRID 05000774) reported testing the effects of two formulations of chlorpyrifos on biota in small (970 liter) plastic lined pools. Pools were prepared as follows: 9 pools with a 5 cm base of soil (sediment); 9 with 5 cm of soil and 70 grams of rabbit ration per week (for high organic material); and 9 with just water (no soil covering the bottom or organic material added). Three of each kind served as untreated controls. Three pools of each kind were treated with 2.5 ppm (11.5% Dursban CPE) and three of each kind were treated with 0.009 ppm (0.48% Dursban WE). At 2.5 ppm, populations of gerrids and larval chaoborids were suppressed for 9 weeks while larval dytiscids populations were suppressed for 11 weeks. Gerrid and larval dytiscids populations were also reduced for 4 and 2 weeks, respectively, at the 0.009 ppm rate.

Siefert (1984, MRID 00154727) treated a natural pond with both granular and EC formulations of chlorpyrifos at 0.05 lb. ai/A. Treatments occurred on June 1 (granular), June 12 (EC) and June 20 (granular). Concentrations remained less than 0.1 ppb until the second application (first EC application) at which time they became measurable at between 0.1 and 0.3 ppb. Decreases in populations of *Simocephalm*, *Paracyclops*, *Hyalella*, Chironomidae, Zygoptera, Ephemeroptera, Anisoptera and *Plea* were seen between the second and third treatments (both EC's). *Hyalella* and *Plea* populations did not recover, however, Zygoptera, Ephemeroptera, and Anisoptera showed signs of recovery 5 to 8 weeks after the last application.

Wallace *et al*. (1973, MRID 05000821) found that 0.1 ppm concentration of chlorpyrifos in streams caused large increases in drift of nontarget aquatic invertebrates. Most of the drifting organisms were dead; however, post-treatment sampling indicated that these organisms were not eradicated.

Washino *et al*. (1972, MRID 00095370) studied the effects of three low volume sprays with Dursban at 0.0125 and 0.0167 lb ai/A at numerous sites using observations of various biotic responses of caged invertebrates and natural invertebrate populations. Specific responses were not associated with specific application rates. However, since they were so close together, it does not detract from the value of the observations made in this study. Caged mayflies and *Laccophilus* spp. were the only invertebrates experiencing mortality.

Chlorpyrifos effects on insects in treated and untreated rice fields

Insect species	Treated rice fields		untreated rice fields	
	No. exposed	% mort.	No. exposed	% mort.
Laccophilus spp. adult	50	32	10	0
Siphlonurus spp. nymphs	30	70	5	0
Total organisms	80	52	10	0

Sampling of invertebrate populations did not result in a consistent pattern of mortality. In some cases, samples in treated fields had more organisms in a taxon than in untreated fields. Taxa collected included *Belostoma* spp., *Corisella* sp., *Hydrophilus triangularis, Tropisternus lateralis, Laccophilus* spp., and *Thermonectus basilaris*.

(c) Summary of Field Studies Results

Direct application field studies do not represent routes of exposure characteristic of spray drift or runoff from agricultural crops. However, results from direct application studies can be used to assess adverse effects on aquatic organisms from agricultural uses. Comparison of EECs from agricultural uses can be matched to measured water concentrations in the field studies and the adverse effects observed at that concentration would be indicative of anticipated effects from exposures due to agricultural uses.

Field studies with aquatic invertebrates show that direct application of rates of 0.01 lb ai/A will impact nontarget invertebrates (Washino *et al*., 1972 and Hurlbert *et al*., 1970 and 1972). Rates of 0.05 lb ai/A reduced populations of nontarget invertebrates (Seifert, 1984). Most of these studies did not provide water depths or residue concentrations. Macek et al. (1972) found that no impact occurred at 0.01 lb ai/A (measured residues of around 0.5 to 1 ppb but that nontarget invertebrate populations were reduced at 0.05 lb ai/A (measured residues of 1.3 to 2.4 ppb). Eaton (1984) found that invertebrate diversity and populations of amphipods in artificial streams were reduced at concentrations of 0.12 to 0.83 ppb (continuous) and 1 to 7 ppb (pulsed every 14 days). Further aquatic field studies are not required.

vii. Reports of Freshwater Incidents

A number of fish kills have been reported for chlorpyrifos. Most incidents are related to perimeter applications around residences. On June 25, 1975, about 500 bream in a Georgia pond were killed when a swimming pool backwashed into the pond. Analysis of a water sample found 1.5 ppm of chlorpyrifos, which was determined as the cause of the kill. Dursban M had been ground sprayed around the residence.

In April 1977, a series of fish kills occurred in a watershed of the Saline River. The fish kills followed years of use, but no recent applications of Dursban and Furadan by a contractor for the Weyerhauser Corporation to treat pine seedlings in the watershed area. One kill included crappie, bass, bullhead, catfish, and redhorse were reported by Arkansas State Pollution Control and Ecology Department in a river at the mouth of a lake. Chlorpyrifos was found in an unidentified sample. Approximately 200 dead fish were found in another kill along the Saline River and Brushy Creek above Dierks Reservoir in Arkansas. About 70 percent were bullhead catfish and 28 percent were redhorse and spotted suckers. One dead flathead catfish and a green sunfish were also found. Several days later similar fish deaths were reported from Camp Creek between Camp Creek Falls and Dierks Reservoir. The incidents occurred after heavy rains 3-4 weeks before and after April 17-20, 1977. Dursban was found in analyses of fish liver and blood (341 ug/kg), bottom sediments (7.15 ug/kg), 0.46 ug/l (ppb) in water collected at the mouth of the Saline River above Dierks Reservoir, and > 0.46 ug/l (ppb) in water from Saline River at Highway 4 bridge. Samples were also checked for furadan, but none was found.

In July 1992, a fish kill of about 2,000 small bluegill was reported in Abbott Lake at Peaks of Otter, Virginia. Two rooms in a motel had been treated for termites with Dursban TC by a commercial certified applicator. It was concluded that the Dursban was unknowingly injected into an underground water supply, which discharged into the lake.

(e) Estuarine and Marine Toxicity

Estuarine and marine testing may be required when an end-use product is intended for direct application to the marine/estuarine environment or is expected to reach this environment in significant concentrations. Chlorpyrifos uses on such major crops as corn, alfalfa, cotton, peanuts, sorghum, soybeans, tobacco, citrus, apples, cranberries, vegetables, wheat and turf/golf courses are likely to expose estuarine areas when used in coastal counties.

i. Estuarine and Marine Fish Toxicity

(a) Estuarine and Marine Fish, Acute Toxicity

The minimum data required on the technical grade of the active ingredient is one estuarine/marine fish toxicity study (preferably sheepshead minnow or a silverside species).

Estuarine/Marine Fish 96-Hour LC50 Toxicity Findings

Surrogate Species	% AI	LC_{50} ppb ai (95 % C.I.)	MRID No. Author/Date	Toxicity Category	Fulfills Guideline Requirement
Tidewater Silverside *Menidia peninsulae* (1-day old larvae) (flow-measured) (static-nominal)	92 %	f-m 0.96 (0.71-1.3) s-n 4.2 (3.3 -5.5)	40228401 Mayer 1986	very highly toxic toxicity greater in flow-thru vs. static	S too small
Tidewater Silverside *Menidia peninsulae* (7-day old larvae) (flow-measured) (static-nominal)	92 %	f-m 0.52 (0.46-0.59) s-n 2.0 (1.5 -2.8)	40228401 Mayer 1986	very highly toxic toxicity greater in flow-thru vs. static	Y

Tidewater Silverside *Menidia peninsulae* (14-day old larvae) (flow-measured) (static-nominal)	92 %	f-m 0.42 (0.33-0.57) s-n 1.8 (1.5 -2.2)	40228401 Mayer 1986	very highly toxic toxicity greater in flow-thru vs. static	Y
Tidewater Silverside *Menidia peninsulae* (28-day old larvae) (flow-measured) (static-nominal)	92 %	f-m 0.89 (0.69-1.1) s-n 3.9 (3.1 -5.8)	40228401 Mayer 1986	very highly toxic toxicity greater in flow-thru vs. static	Y
Tidewater Silverside *Menidia peninsulae* (60-day old juvenile) (flow-measured)	92 %	f-m 1.3 (0.99-1.7)	40228401 Mayer 1986	very highly toxic	Y
Atlantic Silverside *Menidia menidia* (1-day old larvae) (flow-measured) (static-nominal)	92 %	f-m 0.51 (0.40-0.67) s-n 4.5 (3.6 -5.7)	40228401 Mayer 1986	very highly toxic toxicity greater in flow-thru vs. static	S too small
Atlantic Silverside *Menidia menidia* (7-day old larvae) (flow-measured) (static- nominal)	92 %	f-m 1.0 (0.85-1.2) s-n 2.8 (2.3 -3.5)	40228401 Mayer 1986	very highly toxic toxicity greater in flow-thru vs. static	Y
Atlantic Silverside *Menidia menidia* (14-day old larvae) (flow-measured) (static-nominal)	92 %	f-m 1.1 (0.97-1.3) s-n 2.4 (1.9 -2.9)	40228401 Mayer 1986	very highly toxic toxicity greater in flow-thru vs. static	Y
Atlantic Silverside *Menidia menidia* (28-day old larvae) (flow-measured) (static-nominal)	92 %	f-m 3.0 (2.6 -4.0) s-n 4.1 (3.3 -5.2)	40228401 Mayer 1986	very highly toxic toxicity greater in flow-thru vs. static	Y
Atlantic Silverside *Menidia menidia* (53-day old juvenile) (flow-measured)	92 %	f-m 1.7 (1.4 -2.0)	40228401 Mayer 1986	very highly toxic	Y
Atlantic Silverside *Menidia menidia* (adult) (flow-measured)	92 %	f-m 1.7 (1.4 -2.0)	40228401 Mayer 1986	very highly toxic	S age too old
California Grunion *Leuresthes tenuis* (1-day old larvae) (flow-measured) (static-nominal)	92 %	f-m 1.0 (0.82-1.3) s-n 5.5 (2.8 -6.9)	40228401 Mayer 1986	very highly toxic toxicity greater in flow-thru vs. static	S too small
California Grunion *Leuresthes tenuis* (7-day old larvae) (flow-measured) (static-nominal)	92 %	f-m 2.7 (1.9 -5.4) s-n 2.7 (2.0 -3.5)	40228401 Mayer 1986	very highly toxic	Y
California Grunion *Leuresthes tenuis* (14-day old larvae) (flow-measured) (static-nominal)	92 %	f-m 1.0 (0.76-1.4) s-n 1.8 (1.2 -2.5)	40228401 Mayer 1986	very highly toxic toxicity greater in flow-thru vs. static	Y

California Grunion *Leuresthes tenuis* (28-day old larvae) (flow-measured) (static-nominal)	92 %	f-m 1.3 (1.0 -1.7) s-n 2.6 (2.0 -3.7)	40228401 Mayer 1986	very highly toxic toxicity greater in flow-thru vs. static	Y
Inland Silverside *Menidia beryllina* (72-day old juvenile) (flow-measured)	92 %	f-m 4.2 (3.4 -5.4)	40228401 Mayer 1986	very highly toxic	Y
Gulf Killifish *Fundulus grandis* (juvenile) (flow-measured)	92 %	f-m 1.8 (1.5 - 2.1)	40228401 Mayer 1986	very highly toxic	Y
Longnose Killifish *Fundulus similis* (juvenile) (flow-nominal)	92 %	f-n 3.2 (no 95% CL)	40228401 Mayer 1986	very highly toxic	Y
Longnose Killifish *Fundulus similis* (adult) (flow-measured)	92 %	f-m 4.1 (2.8 -6.9)	40228401 Mayer 1986	very highly toxic	S age too old
Striped Mullet *Mugil cephalus* (juvenile) (flow-measured)	92 %	f-m 5.4 (4.0 -6.9)	40228401 Mayer 1986	very highly toxic	Y
Spot *Leiostomus xanthurus* (juvenile) (flow-nominal)	92 %	f-n 7.0 (no 95% CL)	40228401 Mayer 1986	very highly toxic	Y
Sheepshead Minnow *Cyprinodon variegatus* (28-day juvenile) (flow-nominal)	92 %	f-n 270 (240- 300)	40228401 Mayer 1986	highly toxic	Y
Sheepshead Minnow *Cyprinodon variegatus* (juvenile) (flow-nominal)	92 %	f-n > 1000 (no 95% CL)	40228401 Mayer 1986	toxicity undetermined	S
Sheepshead Minnow *Cyprinodon variegatus* (adult) (flow-measured)	92 %	f-m 140 (110-160)	40228401 Mayer 1986	very highly toxic	S age too old
Sheepshead Minnow *Cyprinodon variegatus* (juvenile) (flow-measured)	95 %	f-m > 76 (no effect)	42144904 Surprenant 1989	toxicity undetermined	N
Gulf Toadfish *Opsanus beta* (juvenile) (flow-measured) (static-measured)	92 %	f-m 68 (0 - inf.) s-m 520 (450- 600)	40228401 Mayer 1986	very highly toxic	Y
Striped Bass *Morone saxatilis* (juvenile)	99+ %	0.58	05000819 Korn & Earnest 1974	very highly toxic	S

Acute results indicate that technical grade chlorpyrifos is moderately to very highly toxic to estuarine and marine fish species. Results from flow-through tests with measured test concentrations yielded more toxic values than static, nominal tests. In general, younger life stages are more sensitive than older stages. Several estuarine fish species are more sensitive to chlorpyrifos than bluegill, the most sensitive freshwater species. The guideline requirement for acute testing of the technical grade on estuarine/marine fish is fulfilled.

Degradate: The degradate, TCP, forms a large percent of the recoverable active ingredient in various compartments of the environment. Therefore, a special estuarine fish acute test was required to address concerns about exposures of estuarine fish species.

Degradate Estuarine/Marine 96-Hour LC50 Toxicity Findings

Surrogate Species	% AI	LC_{50} ppm ai (95% CL)	MRID No. Author/Date	Toxicity Category	Fulfills Guideline Requirement
Atlantic Silverside *Menidia menidia* (flow-thru/measured)	99.9 %	58.4 (44.5-76.7)	42245901 Graves & Smith 1991	slightly toxicity	Y

The major degradate of chlorpyrifos (3,5,6-trichloro-2-pyridinol) is slightly toxic to estuarine fish. The requirement for a major degradate acute estuarine fish test is fulfilled.

(b) Estuarine and Marine Fish, Chronic Toxicity

Chronic testing of a pesticide to estuarine and marine fish is required, if the criteria for acute estuarine tests are met and the pesticide is applied multiple times per season and/or is persistent. Chlorpyrifos meets these criteria, hence a chronic estuarine/marine fish early life stage study was required. The minimum data required on the technical grade of the active ingredient is an estuarine/marine fish early life stage toxicity study (preferably sheepshead minnow or a silverside species).

Estuarine/Marine Fish Chronic Toxicity Findings

Surrogate Species	% AI	NOEC/LOEC ppb ai	Toxic Effects	MRID No. Author/Date	Fulfills Guideline Requirements
Tidewater Silverside *Menidia peninsulae* (28-day, flow-meas.)	Tech.	NOEC 0.38 LOEC 0.78	0.38 ppb 42 % red. survival (not sign.) 0.78 ppb 74 % red. survival	00154718 Goodman *et al*. 1985	S raw data unavailable
Atlantic Silverside *Menidia menidia* (28-day, flow-meas.)	Tech.	NOEC 0.28 LOEC 0.48	0.48 ppb 63 % red. survival 32 % red. body weight	00154718 Goodman *et al*. 1985	S raw data unavailable
Inland Silverside *Menidia beryllina* (28-day, flow-meas.)	Tech.	NOEC 0.75 LOEC 1.8	1.8 ppb 49 % red. survival 16 % red. body weight	00154718 Goodman *et al*. 1985	S raw data unavailable

The toxicity results of the three fish early life studies on the three *Menidia* spp. are very similar. The NOECs for the three tests range from 0.28 to 0.75 ppb. The adverse effects were statistically ($P < 0.05$) significant reductions in survival and/or body weight. In the tidewater silverside ELS test, a reduction in fish survival of 42 percent at 0.38 ppb was high, but it is not statistically ($P < 0.05$) significant. Taken together the results of these three studies are sufficient to define the chronic toxicity to estuarine fish. The testing requirement for an estuarine/marine fish is fulfilled.

ii. Estuarine and Marine Invertebrate Toxicity

(a) Estuarine and Marine Invertebrate, Acute Toxicity

The minimum data required on the technical grade of the active ingredient are two estuarine/marine invertebrate toxicity studies (preferably mysid shrimp and eastern oyster, respectively).

Estuarine/Marine Invertebrate 96-Hour EC50/LC50 Toxicity Findings					
Surrogate Species	**% AI**	**LC_{50}/EC_{50} ppb ai (95% CL)**	**MRID No. Author/Date**	**Toxicity Category**	**Fulfills Guideline Requirement**
Mysid Shrimp *Mysidopsis bahia* (1-day old juv.) (flow-measured) (static-nominal)	92 %	f-m 0.035 (0.029-0.043) s-n 0.056 (0.032-0.10)	40228401 Mayer 1986	very highly toxic	Y
Mysid Shrimp *Mysidopsis bahia* (juvenile) (flow-thru/meas.)	95 %	0.045 (0.038-0.070)	42144906 Surprenant 1989	very highly toxic	Y
Brown Shrimp *Penaeus aztecus* (juvenile) (flow-thru, nominal)	92 %	0.20 (no 95% CL)	40228401 Mayer *et al*. 1986	very highly toxic	Y
Grass Shrimp *Palaemonetes pugio* (juvenile) (flow-thru, nominal)	92 %	1.5 (no 95% CL)	40228401 Mayer *et al*. 1986	very highly toxic	Y
Pink Shrimp *Penaeus duorarum* (juvenile) (flow-thru, nominal)	92 %	2.4 (no 95% CL)	40228401 Mayer *et al*. 1986	very highly toxic	Y
Eastern Oyster *Crassostrea virginica* (embryo-larvae) (static-nominal)	92 %	2,000 (1,500-2,800)	40228401 Mayer 1986	very highly toxic	Y
Eastern Oyster *Crassostrea virginica* (shell-deposition) (flow-nominal)	92 %	13ºC 34 28ºC 270	40228401 Mayer 1986	very highly toxic	Y

Supplemental Estuarine/Marine Invertebrate 96-Hour EC50/LC50 Toxicity					
Surrogate Species	**% AI**	**LC_{50}/EC_{50} ppb ai (95% CL)**	**MRID No. Author/Year**	**Toxicity Category**	**Fulfills Guideline Requirement**
Mysid Shrimp *Mysidopsis bahia* (adult) (flow-nominal)	92 %	0.040 (0.030-0.043)	40228401 Mayer *et al*. 1986	very highly toxic	S
Blue Crab *Callinectes sapidus* (juvenile) (flow-nominal)	92 %	5.2 (no 95% CL)	40228401 Mayer *et al*. 1986	very highly toxic	S
Eastern Oyster *Crassostrea virginica* (shell-deposition) (flow-measured)	95 %	84 (77 - 91)	42144905 Surprenant 1989	very highly toxic	S insufficient control shell growth
Eastern Oyster *Crassostrea virginica* (shell-deposition) (flow-nominal)	?? %	0.1 (no 95% CL)	00056603 Lowe 1968	highly toxic	S

Results from the above tests indicate that technical grade chlorpyrifos is classified as very highly toxic to shrimp and to oysters during shell deposition, and highly toxic to larval oysters. The guideline requirement for acute toxicity testing of the technical grade on estuarine and marine invertebrates is fulfilled.

Degradate: The degradate, TCP, forms a large percent of the recoverable active ingredient in various compartments of the environment. Therefore, special estuarine/marine invertebrate acute tests with the degradate was required to address these concerns.

Degradate Estuarine/Marine 96-Hour LC50 Invertebrate Toxicity Findings					
Surrogate Species	**% AI**	**LC_{50} ppm ai (95% CL)**	**MRID No. Author/Year**	**Toxicity Category**	**Fulfills Guideline Requirement**
Grass Shrimp *Palaemonetes pugio* (flow-thru/meas.)	99.9%	83 (71.4 -97)	42245902 Graves & Smith 1991	slightly toxic	Y
Eastern Oyster *Crassostrea virginica* (shell deposition) (flow-thru/meas.)	99.9%	9.3 (3.6- 24.2)	42245903 Holmes & Smith 1991	slightly toxic	Y

Acute studies with estuarine shrimp and oysters indicate that this degradate is slightly and moderately toxic to these species, respectively. This special requirement for major degradate testing has been fulfilled for shrimp and mollusks.

(b) Estuarine/Marine Invertebrate, Chronic Toxicity

Chronic testing of a pesticide to estuarine/marine invertebrates is required, if the criteria for acute estuarine tests are met and the pesticide is applied multiple times per season and/or is persistent. Chlorpyrifos meets all these criteria, hence a chronic estuarine/marine invertebrate life cycle study was required. The minimum data required on the technical grade of the active ingredient is an estuarine/marine invertebrate early life stage toxicity study (preferably mysid shrimp *Mysidopsis bahia*).

Estuarine/Marine Invertebrate Life Cycle Toxicity Findings					
Surrogate Species	**% AI**	**NOEC - LOEC ppb ai**	**Toxic Effects**	**MRID No. Author/Date**	**Fulfills Guideline Requirement**
Mysid Shrimp *Mysidopsis bahia* (flow-though test) (C^{14} measured)	99.7%	NOEC < 0.0046 LOEC 0.0046	0.0046 ppb sign. 85% reduction in number of young	42664901 Sved, Drottar, Swigert & Smith 1993	S Strong solvent effects on production of young

Results from the mysid shrimp life cycle study indicate chronic toxicity to chlorpyrifos at 0.0046 ppb (the lowest test level). Toxicity could be lower since a NOEC was not determined. Statistically ($P < 0.05$) significant reduced number of young and mean number of young per female in solvent controls compared to negative control. The requirement for a chronic estuarine invertebrate test has not been fulfilled, because the solvent caused effects and the test failed to identify a NOEC. A NOEC is necessary to assess the effects of mitigation proposals. Risk assessments can be made with the results of this test, since EECs exceed the lowest test concentration. The value added is high.

iii. Estuarine Behavioral Toxicity

Hansen (1969, MRID 00102758) reported that sheepshead minnows will attempt to avoid concentrations of chlorpyrifos at around 100 ppb. No such avoidance was observed at 10 and 50 ppb.

Hansen *et al*. (1973, MRID 00095363) reported that grass shrimp did not avoid various concentrations of chlorpyrifos (1, 0.1 and 0.01 ppb) when provided with clean water into which they could move. Their movement was, apparently, random. These studies fulfill no guideline requirements, but provide supplemental information.

iv. Estuarine Field Studies

Estuarine field tests with formulated products were required to support the previous registration of chlorpyrifos applied directly to estuarine areas as a mosquito larvicide. Numerous estuarine field studies were conducted with direct application to water prior to the withdrawal of mosquito larvicide uses of chlorpyrifos. The results of these field studies are valuable to assess agricultural risks from spray drift and runoff. The measured concentrations in field studies can be matched to agricultural EECs from crops grown in coastal counties, such as alfalfa, corn, cotton, cranberries, citrus, peanuts, nut crops, and tobacco.

Salt marsh potholes were treated with a 1% granular formulation at 28.03 g ai/hectare (0.025 lb ai/A) (Campbell and Denno 1976, MRID 05000840). Numerous benthic organisms were studied through weekly sampling and identification of organisms. Species richness, diversity and density of insects before and after treatment were used to determine effects. No significant changes or effects to seasonal trends were noted. There were no signs of toxicity observed.

Ludwig *et al*. (1967, MRID 00095130; and 1968, MRID 00095301) studied the effects of aerial applications at 0.025 and 0.05 lb ai/A to shrimp and several fish species. The 0.025 lb ai/A application rate had no obvious effects on caged shrimp nor natural shrimp populations. At 0.05 lb ai/A, brown shrimp populations were greatly reduced between 4 and 24 hours following treatment. At 72 hours, all shrimp were dead. The 0.025 lb ai/A application did not kill caged young of the following fish species: spotted croaker *Leiostomus xanthurus*, sheepshead minnow *Cyprinodon variegatus* and gulf killifish *Fundulus grandis* or mullet *Mugil cephalus*. However, an application of 0.05 lb ai/A caused the following mortality in caged young fish, but no mortality to the caged mullet.

	0.025 lb ai/A			0.05 lb ai/A		
Time after Treatment	% Mortality treat.	% Mortality control	Residues (ppb)	% Mortality treat.	% Mortality control	Residues (ppb)
1 hr.	0	0	2.2-6.4	0	0	3.7-8.7
4 hrs	0	0	0.1-2.2	0	0	0.7-2.8
24 hrs	0	0	< 0.1-0.3	19	0	0.2-0.8
48 hrs	0	0	not rptd	21	0	0.2
72 hrs	0	0	not rptd	34	100	0.1-0.2
7 days	0	0	< 0.1	47	100	< 0.1-0.2
21 days	0	0	not rptd	not rptd		< 0.1

Miller (1966, MRID 00104696) treated two areas of Point Clear Island, Mississippi to determine the effects of aerially-applied chlorpyrifos on fauna of coastal waters. Caged shrimp, fish and crabs were observed. Shrimp, flounder, and possibly silver perch and mollies were adversely affected by application of 0.5% granular chlorpyrifos at 0.018 to 0.069 lb ai/A. All caged shrimp, flounder and silver perch were killed within 48 hours of treatment.

Thirugnanam and Forgash (1977, MRID 44585408) reported that caged mummichogs (*Fundulus heteroclitus*) exposed to four successive applications of chlorpyrifos granules at 0.025 lb ai/A showed AChE inhibition ranging from 56 to 100%. By 24 hours after the second application, 18.6% of the treated fish died. Live fish collected at this time exhibited 96% AChE inhibition.

In 1967, Wall and Marganian (1971, MRID 05000928) tested the effects of 1% granular chlorpyrifos to 0.12 acre intertidal plots on sandy beaches when the tide was out (i.e. to bare sand) at 0.05, 0.1 and 0.2 lb ai/A. All caged organisms were located in front of the treated plots below the low tide level. At the 0.2 lb rate, numerous uncaged killifish (*Fundulus* sp.) were found dead and a few unidentified crabs were found dead the day after treatment. However, caged fish (*Fundulus* sp.) and shrimp (*Palaemonetes* sp.) appeared unaffected for four days after treatment when they were released. No fish mortality was observed following treatment with the two lower rates. At 0.1 lb ai/A, fiddler crabs (*Uca pugnax*) were found dead one and two days following treatment. Other than collembolans (non-target insect) and possibly naidid worms, no apparent reduction of the typical intertidal sand organisms appeared to have occurred. Again caged species were not affected. At 0.05 lb ai/A, adverse effects were not observed. This study is significant because direct application to water did not occur, so except for the fiddler crabs, exposure appears to have occurred with the tidal inflow.

In 1969, Wall and Marganian (1973, MRID 00158261) applied 1% granular chlorpyrifos at low tide to salt marsh plots at 0.05 and 0.2 lb ai/A. Caged fish (*Fundulus* spp.), ribbed mussels (*Modiolus demissus*), *Palaemonetes* sp. and fiddler crabs (*Uca pugnax*) were placed in drainage creeks immediately adjacent to treated tidal flats. At the 0.2 lb ai/A rate, the only observed effect was an apparent reduction in the numbers of *Leptochelia* spp. (an isopod). No impacts to caged organisms were observed during the first two days after treatment, after which time they were released.   However, the report indicates that at 0.05 lb ai/A, seven dead fiddler crabs were observed on one plot (of two) on the day following treatment. Many live, active fiddler crabs were also observed on that day. Caged *Fundulus* spp. were also killed following the 0.05 lb ai/A treatment. No other adverse effects were noted at this rate. Again, these caged organisms were not exposed to direct spray, but to tidal water flowing over treated tidal plots. In a second test on salt marsh for control of *Tabanus lineola* and *T. nigrovittatus* larvae, 1% granular chlorpyrifos was applied at 0.05 lb ai/A. The results were erratic. In one plot, caged *Fundulus* spp. were found dead on the second day following treatment, while in another plot no deaths were found. No other organisms in the treated areas appeared to be directly affected.

Marganian and Wall (1972, MRID 00095367) reported chlorpyrifos residue levels in and affects on fauna collected from treated intertidal sand plots and salt marsh plots on Cape Cod over a three year period, 1967-69). Treatments were made during low tide with 1% chlorpyrifos granules at 0.05, 0.1 and 0.2 lb ai/A. Biota, sand and water were collected for chemical analysis. General observations indicated that 0.1 and 0.2 lb ai/A killed numerous fiddler crabs and numerous insect larvae. Numerous fiddler crabs were killed in the plot treated aerially at 0.05 lb ai/A. Residues recovered in biota included up to 0.43 ppm in gnats, 2.3 ppm in white oligochaetes, 2.58 ppm in ribbed mussels, 4.62 ppm in fiddler crabs, 14 ppm in horseflies and 15.7 ppm in marsh snails.

In summary, estuarine field studies have shown that direct application of 0.05 lb ai/A will kill estuarine minnows and brown shrimp (Ludwig et al., 1986), but that 0.025 lb ai/A did not cause mortality to observed organisms (Ludwig et al., 1968 and Campbell and Denno, 1976, 5000840). Thirugnanam and Forgash (1977, MRID 44585408) found that 0.025 lb ai/A did kill caged mummichogs and reduce their cholinesterase activity by 96%. Application of 0.05 lb ai/A applied to intertidal plots killed uncaged invertebrates and caged fish in subtidal areas adjacent to application sites (Marganian and Wall, 1972 and Wall and Marganian, 1973).

These tests do not fulfill the requirement for testing for agricultural or non-agricultural uses such as citrus, peanuts, cotton, soybeans or wheat. The results do suggest hazard to aquatic invertebrates at expected exposure levels from these other uses. Further field testing requirements are waived at this time.

v. Estuarine Field Incidents and Monitoring Data

Other than examples of chlorpyrifos effects on estuarine mortalities and effects reported in the above field studies, EFED knows of no estuarine field incidents. Only a few fish kills have been alluded to by National Oceanic and Atmospheric Administration (NOAA). However, wide-spread chlorpyrifos contamination exists in estuarine areas. In most cases, chlorpyrifos was found in biota, which agrees with monitoring data of freshwater fish cited above.

NOAA (1992) concluded that chlorpyrifos was responsible for only a few fish kills. However, it was one of the inventoried pesticides found most often in coastal aquatic biota. Chlorpyrifos was reported media in NOAA's data base in EPA's STORET, 1980-1989 included water in Texas and biota in California, Connecticut, Delaware, Florida, Louisiana, Maryland, Massachusetts, Mississippi, New Jersey, New York, Pennsylvania, and Texas. Mussels collected in a mussel watch monitoring along coastal California between 1977 and 1987 contained 2.3-59 ug/kg chlorpyrifos. Sediments in Buzzards Bay, Massachusetts near cranberry bogs contained 245 ug/kg chlorpyrifos. Chlorpyrifos was rated as one of the most hazardous pesticides in NOAA's inventory using the hazard rating system.

f. Plant Toxicity

Testing for toxicity to terrestrial and aquatic plants has not been required for insecticides. When Part 158 of FIFRA is revised, Tier I plant testing will be required. Phytotoxicity testing will be required because of an increased concern for plants in terrestrial and aquatic habitats exposed to pesticides. Plants are vital to the health of the environment and are necessary for the support of nontarget organisms.

i. Terrestrial Plant Toxicity

Testing of terrestrial plants will be required for all insecticides at some future date. The minimum testing required to assess the hazard of a pesticide to terrestrial plants is Tier I seedling emergence tests and vegetative vigor tests on ten crop species tested with typical end-use product(s) at the maximum application rate. Tier II tests are required if toxicity is observed at maximum applications rates in Tier I testing. No Tier I terrestrial plant tests have been received. For Tier I, tests would be required on six dicotyledon and four monocotyledon species. The six dicots are to be at least four different families and the monocots of at least two families. Soybeans, corn, and a dicot root crop like carrot are required species. Preferred test species include: tomato, cucumber, lettuce, soybean, cabbage, carrot, oat, perennial ryegrass, corn, and onion. No testing is currently required to support any chlorpyrifos use.

ii. Aquatic Plant Toxicity

Testing of aquatic plants will be required for all insecticides with outdoor uses at some future date. The minimum testing required to assess the hazard of a pesticide to aquatic plants is Tier I aquatic plant growth tests on four algal species and a vascular aquatic plant. Tier I testing is for typical end-use product(s) and is a maximum dose test. The preferred test species are: *Selenastrum capricortum*, *Skeletonema costatum*, *Anabaena flos-aquae*, a freshwater diatom, and *Lemna gibba* (duckweed).

Tier II (123-2) aquatic plant testing is required, if exposure to nontarget plants is expected and Tier I test results or other information indicate a pesticide will be hazardous at exposure levels.

Aquatic Plant Toxicity Findings

Species	% AI	LC_{50} ppb ai (95% CL)	MRID No. Author/Date	Fulfills Guideline Requirement
Alga *Isochrysis galbana* (static/nominal)	92 %	140	40228401 Mayer 1986	S not a recommended test species
Alga *Thalassiosira pseudonana* (static/nominal)	92 %	150 (120 -180)	40228401 Mayer 1986	S not a recommended test species
Alga *Skeletonema costatum* (static/nominal)	92 %	300 (270 -340)	40228401 Mayer 1986	Y

Tier I aquatic plant studies are not available. Tier II (123-2) algae studies have been received and fulfill the requirement for *Skeletonema costatum*. Based on the toxicity in this algal study, additional Tier II aquatic plant testing is required. Testing is required on the other four Tier II aquatic plant species. Plants are very important in ecosystems and need to be assessed for adverse effects. The value added for additional aquatic plant studies is moderate, because the acute toxicity values for fish and invertebrates are about 100 times more sensitive than for aquatic plants.

iii. Aquatic Plant Field Toxicity

Brown *et al*. (1976, MRID 41063402) tested the effects of direct application of chlorpyrifos on freshwater phytoplankton species. The nominal concentrations tested were 1.2, 2.4, 24 and 240 ppb. The treatment reduced growth of several species (*Ankistrodesmus falcatus*, *Ankistrodesmus spiralis*, *Tetraedron* sp., *Scenedesmus dimorphus*, *Trachelomonas* sp., *Dinobyron* sp., *Glenodinium* sp., *Gonatozygon* sp. and diatoms compared to control growth. Recovery took from 9 to 17 days. *Ceratium* sp. growth was not influenced at any concentration.

Hurlbert *et al*. (1970, MRID 00024400) observed the effects of chlorpyrifos on algae in artificial ponds. Chlorpyrifos was applied 4 times at 2-week intervals directly to artificial ponds at rates ranging from 0.01, 0.05, 0.1 and 1 lb ai/A. Two ponds with a surface area of 27 X 55 feet (10-13 inches deep) were treated at each level. There were two control ponds and two replicates for each of the 4 treatments. The reduction of herbivorous crustaceans apparently stimulated an algal bloom (*Anabaena*). Furthermore, it seems chlorpyrifos did not have an adverse effect on algae in this study.